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ANNUAL REPORTS

ON THE

PROGRESS OF CHEMISTRY.

ANNUAL REPORTS
ON THE
PROGRESS OF CHEMISTRY
FOR 1933.

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TABLE OF ABBREVIATIONS EMPLOYED IN THE REFERENCES.

Abbreviated Title.	FULL TITLE.
A.	Abstracts in Journal of the Chemical Society (until 1925) or in British Chemical Abstracts,* Section A.
Acta Comm. Univ. Tartu.	Acta et Commentationes Universitatis Tartuensis (Dorpatensis).
Acta Phytochim.	Acta Phytochimica.
Acta Sci. Fennicae	Acta Societatis Scientiarum Fennicae.
Amer. Inst. Min. Met. Eng.	American Institute of Mining and Metallurgical Engineers, Technical Publications.
Amer. J. Sci.	American Journal of Science.
Amer. Min.	American Mineralogist.
Anal. Fís. Quím.	Anales de la Sociedad Espanõla Física y Química.
Analyst	The Analyst.
Angew. Chem.	Angewandte Chemie (formerly Zeitschrift für angewandte Chemie).
Annalen	Justus Liebig's Annalen der Chemie.
Ann. agron.	Annales agronomiques.
Ann. Bot.	Annals of Botany.
Ann. Chim.	Annales de Chimie.
Ann. Chim. analyt.	Annales de Chimie analytique et de Chimie appliquée.
Ann. Falsif.	Annales des Falsifications et des Fraudes.
Ann. Inst. Pasteur	Annales de d'Institut Pasteur.
Ann. Inst. Platine	Annales de l'Institut du Platine et des autres Métaux Précieux.
Ann. Inst. Polytech. Leningrad	Annales de l'Institut Polytechnique de Leningrad.
Ann. Physik	Annalen der Physik.
Ann. Physique	Annales de Physique.
Ann. Reports	Annual Reports of the Chemical Society.
Arch. Eisenhüttenw.	Archiv für das Eisenhüttenwesen.
Arch. Elektrotechnik	Archiv für Elektrotechnik.
Arch. Pharm.	Archiv der Pharmazie.
Arch. Phys. biol. Chim.-phys.	Archives de Physique biologique et de Chimie-physique des Corps organisés.
Arch. Sci. phys. nat.	Archives des Sciences physiques et naturelles.
Arch. Suikerind. Ned.-Indië	Archief voor de Suikerindustrie in Nederlandsch-Indië.
Arhiv Hemiju	Arhiv za Hemiju i Farmaciju.
Arkansas Agric. Expt. Sta. Bull.	Arkansas Agricultural Experiment Station Bulletins.
Arkh. Biol. Nauk.	Arkhiv Biologicheskikh Nauk (Archives des Sciences biologiques, U.S.S.R.).
Arkiv Kemi, Min. Geol.	Arkiv för Kemi, Mineralogi och Geologi.
Arkiv Mat., Astron. Fysik	Arkiv för Matematik, Astronomi och Fysik.
Astrophys. J.	The Astrophysical Journal.
Atti R. Accad. Lincei	Atti (Rendiconti) della Reale Accademia Nazionale dei Lincei, classe di scienze fisiche, matematiche e naturali, Roma.
B.	British Chemical Abstracts,* Section B.
Ber.	Berichte der deutschen chemischen Gesellschaft.
Biochem. J.	The Biochemical Journal.
Biochem. Z.	Biochemische Zeitschrift.
Bot. Gaz.	The Botanical Gazette.
Bul. Chim. Soc. Române	Buletinul de Chimie pură si applicată al Societătii Române de Chemie.
Bull. Acad. Polonaise	Bulletin Internationale de l'Académie Polonaise des Sciences et des Lettres.

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* The year is not inserted in references to 1933.

Abbreviated Title.	FULL TITLE.
Bull. Acad. roy. Belg.	Académie royale de Belgique.—Bulletin de la Classe des Sciences.
Bull. Acad. Sci. U.R.S.S.	Bulletin de l'Académie des Sciences de l'Union des Républiques Soviétiques Socialistes.
Bull. Assoc. Chim. Sucr.	Bulletin de l'Association des Chimistes de Sucrerie et de Distillerie.
Bull. Chem. Soc. Japan	Bulletin of the Chemical Society of Japan.
Bull. Inst. Phys. Chem. Res. Tokyo	Bulletin of the Institute of Physical and Chemical Research, Tokyo.
Bull. Soc. chim.	Bulletin de la Société chimique de France.
Bull. Soc. chim. Belg.	Bulletin de la Société chimique de Belgique.
Bull. Soc. Chim. biol.	Bulletin de la Société de Chimie biologique.
Bull. Soc. franç. Min.	Bulletin de la Société française de Minéralogie.
Bull. Wagner Free Inst.	Bulletin of the Wagner Free Institute of Science of Philadelphia.
Bur. Stand. J. Res.	Bureau of Standards Journal of Research.
Canadian J. Res.	Canadian Journal of Research.
Chem. Erde	Chemie der Erde.
Chem. and Ind.	Chemistry and Industry.
Chem. Fabr.	Die Chemische Fabrik.
Chem. Listy	Chemické Listy pro Vědu a Průmysl. Organ de la "Ceská chemická Společnost pro Vědu a Průmysl."
Chem. News	Chemical News.
Chem. Reviews	Chemical Reviews.
Chem. Weekblad	Chemisch Weekblad.
Chem. Zentr.	Chemisches Zentralblatt.
Chem.-Ztg.	Chemiker-Zeitung.
Chim. et Ind.	Chimie et Industrie.
Coll. Czech. Chem. Comm.	Collection of Czechoslovak Chemical Communications.
Coll. Symp. Monographs	Colloid Symposium Monographs.
Compl. Abs. Jap. Chem. Lit.	Abstracts of Japanese Chemical Literature, Complete.
Compt. rend.	Comptes rendus hebdomadaires des Séances de l'Académie des Sciences.
Compt. rend. Soc. Biol.	Comptes rendus hebdomadaires de Séances de la Société de Biology.
Compt. rend. Trav. Lab. Carlsberg	Comptes rendus des Travaux du Laboratoire Carlsberg.
Dansk Tidsskr. Farm.	Dansk Tidsskrift for Farmaci.
Deut. Arch. klin. Med.	Deutsches Archiv für klinische Medizin.
Ernähr. Pflanze	Die Ernährung der Pflanze.
Fortschr. Min., Krist. Petr.	Fortschritte der Mineralogie, Kristallographie und Petrographie.
Gazzetta	Gazzetta chimica italiana.
Geol. För. Förh.	Geologiska Förheningens i Stockholm Fördandlingar.
Georgia Agric. Expt. Sta. Bull.	Georgia Agricultural Experiment Station Bulletins.
Giorn. Chim. ind. appl.	Giornale di Chimica industriale ed applicata.
Helv. Chim. Acta	Helvetica Chimica Acta.
Ind. Chem.	The Industrial Chemist and Chemical Manufacturer.
Ind. chim.	L'Industria chimica, mineraria e metallurgica.
Ind. Eng. Chem.	Industrial and Engineering Chemistry.
Ind. Eng. Chem. (Anal.)	Industrial and Engineering Chemistry: Analytical Edition.
Indian J. Physics	Indian Journal of Physics.
Int. Sugar J.	The International Sugar Journal.
J.	Journal of the Chemical Society.
J. Agric. Chem. Soc. Japan	Journal of the Agricultural Chemical Society of Japan.
J. Agric. Res.	Journal of Agricultural Research.
J. Agric. Sci.	The Journal of Agricultural Science.

Abbreviated Title.	FULL TITLE.
J. Amer. Ceramic Soc.	Journal of the American Ceramic Society.
J. Amer. Chem. Soc.	Journal of the American Chemical Society.
J. Amer. Leather Chem. Assoc.	The Journal of the American Leather Chemists' Association.
J. Amer. Pharm. Assoc.	Journal of the American Pharmaceutical Association.
J. Appl. Chem. Russia	Zhurnal prikladnoi Chimii.
J. Bact.	Journal of Bacteriology.
J. Biol. Chem.	Journal of Biological Chemistry.
J. Cell. Comp. Physiol.	Journal of Cellular and Comparative Physiology.
J. Chem. Physics	The Journal of Chemical Physics.
J. Chim. physique	Journal de Chimie physique.
J. Franklin Inst.	Journal of the Franklin Institute.
J. Gen. Chem. (U.S.S.R.)	Journal of General Chemistry (U.S.S.R.) (formerly chemical part of the Journal of the Physical and Chemical Society of Russia).
J. Ind. Eng. Chem.	Journal of Industrial and Engineering Chemistry (now Industrial and Engineering Chemistry).
J. Indian Chem. Soc.	Quarterly Journal of the Indian Chemical Society.
J. Infect. Dis.	The Journal of Infectious Diseases.
J. Inst. Metals	Journal of the Institute of Metals.
J. Lab. Clin. Med.	The Journal of Laboratory and Clinical Medicine.
J. Landw.	Journal für Landwirtschaft.
J. Opt. Soc. Amer.	Journal of the Optical Society of America.
J. Pharm. Chim.	Journal de Pharmacie et de Chimie.
J. Pharm. Soc. Japan	Journal of the Pharmaceutical Society of Japan (Yakugakuzasshi).
J. Phys. Radium	Journal de Physique et le Radium.
J. Physical Chem.	The Journal of Physical Chemistry.
J. pr. Chem.	Journal für praktische Chemie.
J. Russ. Phys. Chem. Soc.	Journal of the Physical and Chemical Society of Russia (now Journal of General Chemistry, U.S.S.R.).
J. Sci. Instr.	Journal of Scientific Instruments.
J. Soc. Chem. Ind.	Journal of the Society of Chemical Industry.
J. Soc. Chem. Ind. Japan	Journal of the Society of Chemical Industry, Japan (Kōgyō Kwagaku Zasshi).
J. Soc. Leather Trades' Chem.	Journal of the International Society of Leather Trades' Chemists.
J. Text. Inst.	The Journal of the Textile Institute.
Jernk. Ann.	Jernkontorets Annaler.
K. Norske Vidensk. Selsk. Forhandl.	Kongelige Norske Videnskabers Selskabs, Forhandlinger.
K. Svenska Vetenskaps Akad. Handl.	Kongliga Svenska Vetenskaps Akademiens Handlingar.
Klin. Woch.	Klinische Wochenschrift.
Kolloid-Z.	Kolloid-Zeitschrift.
Landw. Jahrb.	Landwirtschaftliche Jahrbücher.
L'Ind. sacc. Ital.	L'Industria saccarifera italiana.
Masloboino Zhir. Dels	Masloboino Zhirovoe Dels (Oil and Fat Industry).
Medd. Centralanst. Försöksv. Jordbruks.	Meddelande från Centralanstalten för Försöksväsendet på Jordbruksområdet.
Mem. Coll. Agric. Kyoto	Memoirs of the College of Agriculture, Kyoto Imperial University.
Mem. Coll. Eng. Kyushu	Memoirs of the College of Engineering, Kyushu Imperial University.
Mem. Coll. Sci. Kyoto	Memoirs of the College of Science, Kyoto Imperial University.
Mem. R. Accad. d'Italia	Memorie della reale Accademia d'Italia.
Metallwirt.	Metallwirtschaft, Metallwissenschaft, Metalltechnik.
Mikrochem.	Mikrochemie.
Min. Mag.	Mineralogical Magazine and Journal of the Mineralogical Society.

Abbreviated Title.	FULL TITLE.
Monatsh.	Monatshefte für Chemie und verwandte Theile anderer Wissenschaften.
Nach. Ges. Wiss. Göttingen	Nachrichten von der Gesellschaft der Wissenschaften zu Göttingen.
Naturwiss.	Die Naturwissenschaften.
Natuurwetensch. Tijds.	Natuurwetenschappelijk Tijdschrift.
New Hamps. Agric. Expt. Sta. Bull.	New Hampshire Agricultural Experiment Station Bulletins.
New Jersey Agric. Expt. Sta. Bull.	New Jersey Agricultural Experiment Station Bulletins.
Norsk Geol. Tidsskr.	Norsk Geologisk Tidsskrift.
Nuovo Cim.	Il Nuovo Cimento.
P.	Proceedings of the Chemical Society.
Papier-Fabr.	Der Papier-Fabrikant.
Perf. & Essent. Oil Rec.	Perfumery and Essential Oil Record.
Pflanzenbau	Wissenschaftliches Archiv für Landwirtschaft. Abteilung A. Pflanzenbau.
Pharm. Acta Helv.	Pharmaceutica Acta Helvetiae.
Pharm. Weekblad	Pharmaceutisch Weekblad.
Pharm. Zentr.	Pharmazeutische Zentralhalle.
Pharm. Ztg.	Pharmazeutische Zeitung.
Phil. Mag.	Philosophical Magazine (The London, Edinburgh and Dublin).
Phil. Trans.	Philosophical Transactions of the Royal Society of London.
Physical Rev.	Physical Review.
Physikal. Z.	Physikalische Zeitschrift.
Phytopath.	Phytopathology.
Planta	Zeitschrift für wissenschaftliche Biologie. Abteilung E. Planta. Archiv für wissenschaftliche Botanik.
Plant Physiol.	Plant Physiology.
Proc. Camb. Phil. Soc.	Proceedings of the Cambridge Philosophical Society.
Proc. Imp. Acad. Tokyo	Proceedings of the Imperial Academy of Japan.
Proc. Indiana Acad. Sci.	Proceedings of the Indiana Academy of Science.
Proc. K. Akad. Wetensch. Amsterdam	Koninklijke Akademie van Wetenschappen te Amsterdam.
Proc. Nat. Acad. Sci.	Proceedings of the National Academy of Sciences.
Proc. Physical Soc.	Proceedings of the Physical Society of London.
Proc. Roy. Soc.	Proceedings of the Royal Society.
Proc. Roy. Soc. Edin.	Proceedings of the Royal Society of Edinburgh.
Proc. Soc. Exp. Biol. Med.	Proceedings of the Society for Experimental Biology and Medicine.
Proc. Tech. Sect. Paper Makers' Assoc.	Proceedings of the Technical Section, Paper Makers' Association of Great Britain and Ireland.
Proc. Univ. Durham Phil. Soc.	Proceedings of the University of Durham Philosophical Society.
Przemysł Chem.	Przemysł Chemiczny.
Rec. trav. chim.	Recueil des travaux chimiques des Pays-Bas et de la Belgique.
Rep. Brit. Assoc.	Reports of the British Association for the Advancement of Science.
Rev. Mod. Physics	Reviews of Modern Physics.
Rev. Sci. Instr.	Review of Scientific Instruments.
Rocz. Chem.	Roczniki Chemji organ Polskiego Towarzystwa Chemicznego.
Sci. Papers Inst. Phys. Chem. Res. Tokyo	Scientific Papers of the Institute of Physical and Chemical Research, Tokyo.
Sci. Proc. Roy. Dublin Soc.	Scientific Proceedings of the Royal Dublin Society.
Sci. Rep. Tôhoku Imp. Univ.	Scientific Reports, Tôhoku Imperial University.
Sitzungsber. Akad. Wiss. Wien	Sitzungsberichte der Akademie der Wissenschaften in Wien.

Abbreviated Title.	FULL TITLE.
Sitzungsber. preuss. Akad. Wiss. Berlin	Sitzungsberichte der preussischen Akademie der Wissenschaften zu Berlin.
Strahlenther.	Strahlentherapie: Mitteilungen aus dem Gebiete der Behandlung mit Roentgenstrahlen, Licht und Radioaktiven Substanzen.
Soil Sci.	Soil Science.
Svensk Kem. Tidskr.	Svensk Kemisk Tidskrift.
Tidsskr. Kjemi Berg.	Tidsskrift for Kjemi og Bergvaesen.
Tottori Agric. Coll. Sci. Papers	Tottori Agricultural College, Scientific Papers.
Trans. Amer. Electrochem. Soc.	Transactions of the American Electrochemical Society.
Trans. Faraday Soc.	Transactions of the Faraday Society.
Trans. Opt. Soc.	Transactions of the Optical Society.
Wiss. Veröff. Siemens-Konz.	Wissenschaftliche Veröffentlichungen aus dem Siemens-Konzern.
Z. anal. Chem.	Zeitschrift für analytische Chemie.
Z. angew. Chem.	Zeitschrift für angewandte Chemie (now Angewandte Chemie).
Z. anorg. Chem.	Zeitschrift für anorganische und allgemeine Chemie.
Z. Biol.	Zeitschrift für Biologie.
Z. Elektrochem.	Zeitschrift für Elektrochemie (und angewandte physikalische Chemie).
Z. Krist.	Zeitschrift für Kristallographie.
Z. Metallk.	Zeitschrift für Metallkunde.
Z. Pflanz. Düng.	Zeitschrift für Pflanzenernährung und Düngung.
Z. Physik	Zeitschrift für Physik.
Z. physikal. Chem.	Zeitschrift für physikalische Chemie, Stöchiometrie und Verwandtschaftslehre.
Z. physiol. Chem.	Hoppe-Seyler's Zeitschrift für physiologische Chemie.
Z. Unters. Lebensm.	Zeitschrift für Untersuchung der Lebensmittel.
Zentr. Bakt. Par.	Zentralblatt für Bakteriologie, Parasitenkunde und Infektionskrankheiten.

ERRATA.

VOL. 29, 1932.

Page	Line	
269	7—10*	*for* "The presence of glutathione in plant organs during active vegetative growth is also recorded in an examination of *Obelia* by E. J. Lund,[89] who reports maximum accumulations in the active tips of stems and roots." *read* "The presence of glutathione in plant organs during active vegetative growth is recorded by E. J. Lund.[89] Also in *Obelia* an accumulation of glutathione is indicated in the apical ends of the stems."
287	3*	*for* "has suggested" *read* "criticises the suggestion."

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* From bottom.

ANNUAL REPORTS
ON THE
PROGRESS OF CHEMISTRY.

GENERAL AND PHYSICAL CHEMISTRY.

THE plan of dealing with a limited number of special subjects has again been followed this year. Regret must therefore be expressed that many important contributions to physical chemistry go unmentioned. The advantage of a certain continuity of treatment seems, however, too great to be sacrificed even to an attempt at comprehensiveness. The great achievements in sub-atomic physics are not dealt with in this section since this year there is a special section devoted to such matters, but work on the heavier isotope of hydrogen is dealt with under the heading electrochemistry, in connexion with the electrochemical method of concentrating the heavier isotope in water. The discussions of solubility phenomena and of spectroscopic terms from a general point of view are matters already perhaps overdue. Some pages have once again been devoted to chemical kinetics, but since the scope of the subject has been interpreted rather elastically, it may be hoped that its representation is not out of proportion to the amount of activity which has been displayed in that field. C. N. H.

1. SOLUBILITY AND RELATED PHENOMENA.

The experimental work treated in this section deals in general with the equilibrium of a given molecular species between two phases, *i.e.*, partition coefficients. In the particular case when one of the phases is a pure solid or liquid, we are dealing with solubility in the usual sense of the word, and if one of the phases is gaseous the problem is one of partial or total vapour pressure. From a theoretical point of view there is no distinction between these cases.

The chief interest of such measurement lies in their relation to the forces of attraction and repulsion between molecules, which are theoretically predictable in some simple cases. The fact that a species i is in equilibrium between two phases at constant temperature and pressure is most conveniently expressed by the equality of the partial molal free energies (or chemical potentials) $\overline{F}_i$ of the species in the two phases. For any dilute fluid phase we can write

$$\overline{F}_i - \overline{F}_i^{00} = \overline{F}_i^{0} + RT \log c_i + RT \log f_i \quad . \quad . \quad (1)$$

where $\overline{F}_i^{00}$ refers to an arbitrary standard state of the pure component i, and hence depends only on T, while $\overline{F}_i^{0}$ depends only upon T and the constituents of the phase; c_i is the concentration and f_i the activity coefficient. It is convenient to divide the problem into two parts: (*a*) The value of $\overline{F}_i^{0}$ in different media, *i.e.*, the distribution of a solute between two infinitely dilute phases, and (*b*) the value of f_i in relatively dilute solutions. The two problems become inseparable for concentrated solutions, but can be treated separately for many purposes.

We shall treat first recent work on the so-called solubility of vapours in compressed gases. The activity of any component in a condensed phase varies with the total pressure according to the equation $\partial \log a_A/\partial P = \bar{v}_A/RT$, where $\bar{v}_A$ is the partial molal volume of A in the condensed phase. If the pressure is applied by means of a second gas B, the mole fraction of A in the gas phase will be proportional to its activity only as long as the interaction between A and B is negligible. For all real cases the attractions between A and B lead to a concentration of A much higher than that calculated from the gas laws. This effect, which depends upon the nature of B, can be considered as a solubility of A in compressed B, and may prove of great value for obtaining information about forces between unlike molecules. The first work of this kind is due to F. Pollitzer and E. Strebel,[1] who measured the concentration of vapour in equilibrium with liquid water and carbon dioxide in presence of various gases up to 200 atmospheres pressure. Subsequent investigations have been carried out by A. T. Larson and C. A. Black [2] (liquid ammonia in presence of nitrogen mixtures up to 1000 atmospheres), E. P. Bartlett [3] (water in presence of $N_2 + 3H_2$ up to 1000 atmospheres), E. Lurie and L. J. Gillespie [4] ($BaCl_2,8NH_3$ in nitrogen up to 60 atmospheres), A. Eucken and F. Bresler [5] (carbon disulphide in various gases up to 80 atmospheres), and H. Braune and F. Strassmann [6] (iodine in carbon dioxide up to 50 atmospheres).

---

[1] *Z. physikal. Chem.*, 1924, **110**, 768; *A.*, 1925, ii, 104; see also I. R. McHaffie, *Phil. Mag.*, 1926, [vii], **1**, 561; *A.*, 1926, 355.

[2] *J. Amer. Chem. Soc.*, 1925, **47**, 1015; *A.*, 1925, ii, 501.

[3] *Ibid.*, 1927, **49**, 65; *A.*, 1927, 207.

[4] *Ibid.*, p. 1146; *A.*, 1927, 616.

[5] *Z. physikal. Chem.*, 1928, **134**, 230; *A.*, 1928, 828.

[6] *Ibid.*, 1929, **143**, 225; *A.*, 1929, 1229.

M. Randall and B. Sosnick [7] have shown how activity coefficients can be calculated from results of this kind, and A. Eucken and F. Bresler [8] have treated their results in terms of the van der Waals equation. They find approximate confirmation of Berthelot's relation $a_{12} = \sqrt{a_{11}a_{22}}$ between the attraction constants. F. London [9] has recently given a theoretical treatment of the dispersion forces between unlike molecules and arrives at a similar relation.

The molecular model which has attracted most attention in the theory of solution is that of the ion considered as a sphere with a charge at its centre. The corresponding simplification for the solvent is to consider it as a continuous medium possessing the macroscopic dielectric constant of the solvent. M. Born [10] was the first to consider the electrostatic energy of such a system; he showed that in transferring an ion from a medium A to a medium B, the electrical work is given by

$$F_e = (\varepsilon^2/2r)(1/D_A - 1/D_B) \quad . \quad . \quad . \quad . \quad (2)$$

where ε and r are the charge and radius of the ion, and D_A and D_B the dielectric constants of the media.[11] This result is obviously allied to the well-known fact that salts are more soluble in liquids of higher dielectric constant, and that this effect is more marked for multiply charged ions. Considerable difficulties arise, however, in relating F_e to the quantities in equation (1). For equilibrium distribution of a solute between two phases A and B, $\bar{F}_A = \bar{F}_B$, and equation (1) gives

$$\bar{F}_A{}^0 - \bar{F}_B{}^0 = - RT \log c_A/c_B \quad . \quad . \quad . \quad . \quad (3)$$

It is natural at first sight to equate this difference to F_e in equation (2). However, if A and B are different solvents the value of c_A/c_B depends upon the concentration scale used [12] (*e.g.*, whether we choose mole fractions or volume concentrations), and hence equation (3) needs further justification. Attempts have been made [13] to justify the use of a particular concentration scale in equation (3), but it is necessary to depart from strict thermodynamics, and the assumptions made are of doubtful validity. (Considerations of this kind will, of course, apply to any comparison between thermodynamic data and molecular models.)

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[7] *J. Amer. Chem. Soc.*, 1928, **50**, 967; *A.*, 1928, 588.

[8] *Loc. cit.*; see also J. J. van Laar, *Z. physikal. Chem.*, 1929, **145**, 207; *A.*, 1930, 161.

[9] *Z. physikal. Chem.*, 1930, **11**, [*B*], 221; *A.*, 1931, 149.

[10] *Z. Physik*, 1920, **1**, 45; *A.*, 1921, ii, 166; see *Ann. Reports*, 1926, **23**, 29.

[11] It should be noted that both Born and Fajans interpret the value of the above expression as the "heat of solution of the ions," *i.e.*, the *total* energy change. The nature of the process involved makes it, however, certain that the quantity obtained is the *free* energy—see, *e.g.*, N. Bjerrum and E. Larsson, *Z. physikal. Chem.*, 1927, **127**, 358; *A.*, 1927, 828.

[12] See R. P. Bell, *J.*, 1932, 2906; *A.*, 127.

[13] See, *e.g.*, O. Gatty and A. Macfarlane, *Phil. Mag.*, 1932, **13**, 292; *A.*, 1932, 227.

We can, however, proceed as follows in evaluating the electrical contribution to the work of transfer. Consider distribution of the ion deprived of its charge between the two phases, and let the equilibrium concentrations be (c_A) and (c_B). Then as before

$$(\bar{F}_A^0) - (\bar{F}_B^0) = -RT \log (c_A)/(c_B)$$

and hence

$$\{\bar{F}_A^0 - (\bar{F}_A^0)\} - \{\bar{F}_B^0 - (\bar{F}_B^0)\} = -RT\left\{\log\frac{c_A}{c_B} - \log\frac{(c_A)}{(c_B)}\right\} \qquad (4)$$

$$= -RT\left\{\log\frac{c_A}{(c_A)} - \log\frac{c_B}{(c_B)}\right\}$$

For dilute solutions this expression is independent of the units in which c_A and c_B are expressed, and can be legitimately equated to F_e in equation (2). The concept of "an ion without its charge" is of course somewhat artificial, and it is obviously not in general possible to obtain experimentally (c_A) and (c_B) in equation (4). There is, however, sufficient similarity between some classes of ions and uncharged molecules to make this method of value.

N. Bjerrum and E. Larsson[14] calculated the distribution coefficients of a number of ions between ethyl alcohol and water, partly from existing solubility data, and partly from measurements of *E.M.F.* by E. Larsson.[15] They showed that equations (2) and (3) lead in many cases to reasonable values for the ionic radii. They found, however, that for large organic ions the effect of the hydrocarbon part of the ion was of great importance, and that solvation must be taken into account in other cases. F. K. V. Koch[16] found that a similar treatment of the solubilities of the silver halides in water and the alcohols gave ionic radii agreeing with the crystal lattice values, but that in other solvents there was no relation between the dielectric constant and the free energies of transfer. A. Macfarlane and (Sir) H. Hartley[17] found a general qualitative agreement between the Born equation and the free energies of transfer (calculated from *E.M.F.* measurements) in water and methyl and ethyl alcohols, and similar results were obtained by Brönsted for the solubilities of a number of cobaltammines in water and methyl alcohol.[18] Analogous conclusions have been reached from a study of the effect of added non-electrolyte upon the solubility of salts.[19] It is found that the results lead to feasible values for the ionic radii, but that the effect depends upon the nature of the added electrolyte as well as upon its dielectric constant. All the authors mentioned in this paragraph have neglected (deliberately or implicitly) all "non-electrical" contributions to the work of transfer and used equation (3) with volume concentrations.

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[14] *Z. physikal. Chem.*, 1927, **127**, 358; *A.*, 1927, 828.

[15] Diss., Lund, 1927.

[16] *J.*, 1930, 1551; *A.*, 1930, 1107; *J.*, 1928, 269; *A.*, 1928, 230.

[17] *Phil. Mag.*, 1932, **13**, 425; *A.*, 1932, 230. Cf. also A. E. Brodsky, *Physikal. Z.*, 1929, **30**, 665; *A.*, 1929, 1391.

A. Lannung [20] has measured the solubility of the rare gases in a number of solvents, and the solubility of the alkali halides in acetone. Bjerrum [21] has made use of the great similarity between the rare gases and the alkali and halogen ions to deduce from Lannung's results the electrical part of the free energy of transfer, and to compare it with equation (2). The alkali halides are appreciably soluble in only a very limited number of solvents: in this respect the tetraethylammonium halides offer greater possibilities. Bjerrum and E. Józefowicz [22] have measured the solubility of these salts in a number of solvents ranging from benzene to water. As an uncharged analogue of the tetraethylammonium ion they have measured the distribution of tetraethylsilane [23] between the vapour phase and the solvents employed.

In treating these results, Bjerrum [24] has employed crystal-lattice energies, the Nernst heat theorem, and the Born equation to derive an expression for the solubility of the solid in terms of the ionic radii. By equating this expression to the observed solubility, values are obtained for the ionic radii, which may be compared with the crystal lattice radii. The values obtained are all greater than the lattice radii, and vary from solvent to solvent. The general conclusion is that the Born equation gives a qualitative picture of the results in solvents of similar chemical types (*e.g.*, water and the alcohols), but fails when applied to a large range of solvents. This failure is obviously due to the inadequacy of the picture employed—in particular, the replacement of the solvent by a continuous dielectric, and the neglect of solvation.[25] The discrepancies are particularly marked when water is compared with solvents of very different chemical type, *e.g.*, hydrogen fluoride, hydrogen cyanide, and liquid ammonia.[26] This has been emphasised especially by K. Fredenhagen,[27] who considers that the electrostatic picture should be entirely abandoned in favour of the conception of the chemical solvation of ions. Fredenhagen's own treatment of solution equilibrium is, however, open to serious criticism.[28]

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[18] J. N. Brönsted, A. Delbanco, and K. Volqvartz, *Z. physikal. Chem.*, 1932, **162**, [*A*], 1932; *A.*, 26.

[19] See V. K. LaMer and F. H. Goldman, *J. Amer. Chem. Soc.*, 1931, **53**, 473; *A.*, 1931, **419**; B. B. Owen, *ibid.*, 1933, **55**, 1922; *A.*, 670; C. F. Failey, *ibid.*, 1933, **55**, **4374**.

[20] *J. Amer. Chem. Soc.*, 1930, **52**, 68; *A.*, 1930, 406; *Z. physikal. Chem.*, 1932, **161**, [*A*], 235; *A.*, 1932, 1197.

[21] *Trans. Faraday Soc.*, 1927, **23**, 445; *A.*, 1927, 1028; cf. also ref. (24).

[22] *Z. physikal. Chem.*, 1932, **159**, [*A*], 194; *A.*, 1932, 457.

[23] The true analogue of the $N(C_2H_5)_4^{\cdot}$ ion is $C(C_2H_5)_4$: this is, however, very difficult to prepare.

[24] Chemistry at the Centenary Meeting of the British Association, 1931, p. 34.

A particularly ingenious attempt to eliminate the "non-electrical" factor is due to J. N. Brönsted,[29] who measured the solubility in nine solvents of the salt

$$[Co(NO_2)_2(NH_3)_4]^{\cdot}[Co(NO_2)_4(NH_3)_2]'$$

and of the isomeric non-electrolyte $Co(NO_2)_3(NH_3)_3$. The ratio of the solubility of these two substances depends qualitatively on the dielectric constant in the manner predicted by the Born equation, but there is nothing like quantitative agreement.

Since there is a thermodynamic connexion between the chemical potentials of the components of a mixture, the Born picture of an electrolytic solution can also be employed to calculate the effect of electrolytes upon the solubility of non-electrolytes. This is known as the salting-out effect, and was last dealt with in these Reports in 1926,[30] since when the theory has been worked out in greater detail by P. Debye[31] and P. Gross,[32] and a large number of experimental investigations have been carried out.[33] Reviews and discussions of experimental data have been given by M. Randall and C. F. Failey,[34] G. Scatchard,[35] and P. M. Gross.[36]

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[25] Cf. the evidence obtained from ionic mobilities, *Ann. Reports*, 1930, **27**, 326.

[26] For recent solubility measurements in these solvents, see K. Fredenhagen, *Z. physikal. Chem.*, 1927, **128**, 1; *A.*, 1927, 936; Fredenhagen and G. Cadenbach, *ibid.*, 1930, **146**, [*A*], 254; *A.*, 1930, 421; Fredenhagen, *ibid.*, 1933, **164**, [*A*], 176; *A.*, 566; *Z. anorg. Chem.*, 1930, **186**, 1; *A.*, 1930, 537; P. A. Bond and M. V. Stowe, *J. Amer. Chem. Soc.*, 1931, **53**, 30; *A.*, 1931, 297; A. J. Schattenstein and A. Monossohn, *Z. anorg. Chem.*, 1932, **207**, 204; *A.*, 1932, 990; H. Hunt, *J. Amer. Chem. Soc.*, 1932, **54**, 3509; *A.*, 1932, 1197; Hunt and L. Boncyk, *ibid.*, 1933, **55**, 3528; *A.*, 1112; M. Linhard and M. Stephan, *Z. physikal. Chem.*, 1933, **163**, [*A*], 185; **167**, [*A*], 87; *A.*, 456.

[27] *Z. physikal. Chem.*, 1927, **128**, 1; *A.*, 1927, 936; *ibid.*, 1928, **134**, 33; *A.*, 1928, 1316; *ibid.*, 1929, **140**, [*A*], 65, 435; *A.*, 1928, 397, 513; *ibid.*, 1929, **141**, [*A*], 195; *A.*, 1929, 648; *ibid.*, 1931, **152**, [*A*], 321; *A.*, 1931, 430; *Z. anorg. Chem.*, 1930, **186**, 1; *A.*, 1930, 537.

[28] See H. Hammerschmid and E. Lange, *Z. physikal. Chem.*, 1931, **155**, 85; *A.*, 1931, 1010; *ibid.*, 1932, **159**, 100; *A.*, 1932, 467.

[29] Chemistry at the Centenary Meeting of the British Association, 1931, p. 39.

[30] *Ann. Reports*, 1926, **23**, 28.

[31] *Z. physikal. Chem.*, 1927, **130**, 56; *A.*, 1927, 1141.

[32] *Monatsh.*, 1929, **53**, 445; *A.*, 1930, 150.

If the dielectric constant D of the solution is a linear function of the concentration m of the non-electrolyte, *i.e.*,

$$D = D_0(1 - \beta m) \quad . \quad . \quad . \quad . \quad . \quad (5)$$

(where D_0 is the dielectric constant of the pure solvent, and β a constant), then Debye's theory leads to the expression

$$s = s_0(1 - \sigma\gamma) \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

where s_0 is the solubility of the non-electrolyte in pure solvent, and s its solubility in salt solution of concentration γ. The constant σ is a complicated function of the valencies of the ions, the dielectric constant, the temperature, the constant β in equation (5), and the mean radius of the ions. It is again found that when the experimental data are inserted in this equation, feasible values are obtained for the ionic radii, but that both the non-electrolytes and the electrolytes exhibit individualities not predicted by the simple theory.[37] Most electrolytes decrease the dielectric constant of water, so that both β and σ in equations (5) and (6) are positive quantities, and the solubilities should decrease on addition of electrolyte. This is, of course, the usual salting-out effect, and it is of particular interest to note that Gross, Schwarz, and Iser[38] found that the solubility of hydrogen cyanide (which *increases* the dielectric constant of water) is *increased* by the addition of salt, *i.e.*, it is " salted in."

In the absence of a net electric charge on a molecule, the simplest distribution is that of a dipole, and it is also possible in this case to calculate the electrostatic work of transfer of a molecule from one medium to another by making simplifying assumptions.[39] This theory has been applied to the heat of solution of water in different solvents (calculated from solubility measurements at different temperatures) and agrees approximately with experiment.[40] All other contributions to the work of transfer are neglected, which is only permissible when the dipole energy is large, *i.e.*, when the dipole moment is high and the radius of the molecule small. Martin and his collaborators [41] have measured the partial vapour pressures of mixtures of benzene with some of its polar derivatives, and have interpreted their results in terms of the dipole energy of the molecules in different media. The effects observed are, however, small, and (as the authors themselves realise) it is not legitimate to neglect other factors in this case.

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[33] See, *e.g.*, K. Endo, *J. Chem. Soc. Japan*, 1926, **47**, 374; *A.*, 1926, 729 (phenol); W. Herz and E. Stanner, *Z. physikal. Chem.*, 1927, **128**, 399; *A.*, 1927, 1020 (various substances); S. Glasstone and W. R. Hodgson, *J.*, 1927, 635; *A.*, 1927, 416 (aniline); J. S. Carter and R. K. Hardy, *J.*, 1928, 127; *A.*, 1928, 243 (*m*-cresol); N. Schlesinger and W. Kubasowa, *Z. physikal. Chem.*, 1929, **142**, 25; *A.*, 1929, 874 (ethyl acetate); G. Claxton and H. M. Dawson, *Proc. Leeds Phil. Soc.*, 1929, **1**, 416; *A.*, 1929, 996 (phenol); K. Linderström-Lang, *Compt. rend. Trav. Lab. Carlsberg*, 1929, **17**, No. 13; *A.*, 1929, 1139 (quinol and benzoquinone); E. F. Chase and M. Kilpatrick (jun.), *J. Amer. Chem. Soc.*, 1931, **53**, 2889; *A.*, 1931, 1010; E. Larsson, *Z. physikal. Chem.*, 1930, **148**, [*A*], 148, 307; *A.*, 1930, 995; *ibid.*, 1931, **153**, [*A*], 299; *A.*, 1931, 431 (benzoic acid); P. Gross, *ibid.*, 1929, **6**, [*B*], 215; *A.*, 1930, 989 (dichloroethane and -propane); Gross, K. Schwarz, and M. Iser, *Monatsh.*, 1930, **55**, 287, 329; *A.*, 1930, 989 (acetone and hydrogen cyanide).

[34] *Chem. Reviews*, 1927, **4**, 271.

[35] *Ibid.*, **3**, 383; *Trans. Faraday Soc.*, 1927, **23**, 455; *A.*, 1927, 1028.

[36] *Chem. Reviews*, 1933, **13**, 91.

[37] See specially P. M. Gross, *loc. cit.*, ref. (36).

[38] *Loc. cit.*, ref. (33).

In the majority of liquid mixtures the most important forces are no doubt the so-called van der Waals or dispersion forces, which do not depend upon any permanent charge configurations in the molecules.[42] These forces can be calculated theoretically in simple cases, and the results of such calculations have been applied with some success to the equation of state of gases.[43] It is not yet possible to apply the theory quantitatively to solutions, on account of the complex spatial distribution of the molecules, but in some cases interesting comparisons can be made between pairs of molecules or series of similar compounds. For instance, J. N. Brönsted [44] has introduced the conception of " isochemical " series of molecules, *i.e.*, molecules which differ essentially in size but not in chemical nature. Examples of this are the higher normal hydrocarbons, ethyl valerate and ethyl sebacate, etc. It is reasonable to suppose that in such a series the work of transfer between two given phases is additive for different parts of the molecule, *e.g.*, the value for $C_{16}H_{34}$ should be twice that for C_8H_{18}; similarly the value for $CO_2Et\cdot(CH_2)_8\cdot CO_2Et$ should be twice that for $CH_3\cdot(CH_2)_3\cdot CO_2Et$.

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[39] *Ann. Reports*, 1931, **28**, 39; see also A. R. Martin, *Phil. Mag.*, 1929, **8**, 550; *A.*, 1929, 1389; *Nature*, 1931, **128**, 456; *A.*, 1931, 1222; J. N. Brönsted, *loc. cit.*, ref. (29).

[40] R. P. Bell, *J.*, 1932, 2905; *A.*, 127.

[41] A. R. Martin and B. Collie, *J.*, 1932, 2658; *A.*, 1932, 1197; Martin and C. M. George, *J.*, 1933, 1413.

[42] See *Ann. Reports*, 1930, **27**, 17.

[43] See F. London, *loc. cit.*, ref. (9); J. C. Slater and J. G. Kirkwood, *Physical Rev.*, 1931, [ii], **37**, 682; *A.*, 1931, 675; K. Wohl, *Z. physikal. Chem.*, 1928, **133**, 305; *A.*, 1928, 827; *ibid.*, 1929, **2**, [*B*], 77; *A.*, 1929, 251; *ibid.*, 1931, Bodenstein Festband, 807; *A.*, 1931, 1222; *ibid.*, 1931, **14**, [*B*], 36; *A.*, 1931, 1216; G. Briegleb, *ibid.*, 1933, **23**, [*B*], 105; *A.*, 1231.

[44] *Z. physikal. Chem.*, 1931, Bodenstein Festband, 257; *A.*, 1931, 1221.

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Brönsted[45] adduces a certain amount of experimental support for this principle from measurements of solubility and vapour pressure. The principle should be more rigidly true in the extreme case of colloid particles of different sizes. Similar ideas underlie I. Langmuir's "principle of independent surface action,"[46] according to which the potential energy of a molecule in a liquid is composed additively of the interactions at the different parts of the "interface" between the molecule and its surroundings. J. A. V. Butler[47] has recently found an approximate confirmation of Langmuir's theory in his results for the vapour pressures and solubilities of the normal aliphatic alcohols in water. There appears to be a constant increment in the work of transfer for each CH_2 group added.

So far, we have only considered dilute solutions, and have neglected the solute–solute intermolecular forces which account for the term $RT \log f_i$ in equation (1). In principle, it should be possible to deduce this term from the theory of different types of intermolecular forces, and hence to develop a general theory of the departure of more concentrated solutions from their behaviour at infinite dilution. Actually, however, it is only for long-range forces that it is possible to separate the terms solute–solute, solvent–solvent, and solute–solvent interaction without a precise knowledge of the statistical distribution of the molecules in the liquid. The only long-range forces which we meet with in practice are interionic forces, and hence it is only for electrolyte solutions that this problem has been treated with much success. The original theory of the thermodynamics of electrolyte solutions was that of Debye and Hückel, last treated in these reports in 1927.[48] Since then a great deal of work has been done in examining the theoretical basis of the original theory, in extending it to more concentrated solutions, and in testing the theory experimentally.

The original derivation of the Debye–Hückel expression involved (besides the idealised model of an ionic solution employed) the following approximations or assumptions.

(*a*) The potential of the ionic atmosphere round any ion obeys the Poisson–Boltzmann differential equation,

$$\frac{\partial^2\Psi}{\partial x^2} + \frac{\partial^2\Psi}{\partial y^2} + \frac{\partial^2\Psi}{\partial z^2} = -\frac{4\pi}{D}\sum_i n_i e_i e^{-e_i\Psi/kT} \quad . \quad . \quad (7)$$

where Ψ is the mean potential at any point and n_i is the mean number of ions of charge e_i per c.c.

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[45] J. N. Brönsted and E. Warming, *Z. physikal. Chem.*, 1931, **155**, [*A*], 343; *A.*, 1931, 1119.

[46] *Coll. Symp. Monographs*, 1925, **3**, 48.

[47] *Proc. Roy. Soc.*, 1932, [*A*], **135**, 366; *A.*, 1932, 459; J. A. V. Butler, D. W. Thomson, and W. H. Maclennan, *J.*, 1933, 674; *A.*, 772.

[48] *Ann. Reports*, 1927, **24**, 22; 1926, **23**, 21; 1925, **22**, 27.

(*b*) The distribution of charge round any two ions is the sum of the charges which would be induced by the ions separately.

(*c*) In solving the differential equation (7), it is assumed that

$$e_i\Psi/kT \ll 1 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

Much work has been done in examining these fundamental points in the Debye–Hückel theory. R. H. Fowler[49] was the first to point out that equation (7) might be only an approximation, but concluded that the "fluctuation terms" could be neglected in dilute solution. L. Onsager[50] has shown that assumptions (*a*) and (*b*) above are not in general self-consistent except in very symmetrical cases. However, these difficulties disappear in solutions so dilute that equation (8) is true and the original Debye–Hückel limiting law holds. Valuable confirmation of this is afforded by the work of H. A. Kramers,[51] who has treated the problem from the standpoint of general statistical mechanics without introducing the Poisson–Boltzmann relation. In order to obtain convergent series in the mathematical treatment, it is necessary to assign finite radii to the ions. Kramers shows, however, that in sufficiently dilute solution the activity coefficient is independent of the ionic radii, and at infinite dilution his expression becomes identical with the simple Debye–Hückel equation. The correctness of the latter equation as a limiting law at infinite dilution is thus confirmed by several lines of critical examination.[52]

Matters are much more complicated for concentrated solutions, since the assumptions of the original derivation no longer hold in this case. In particular, assumptions (*a*) and (*b*) above become mutually exclusive (except in certain symmetrical cases).[53] From a purely theoretical point of view it is therefore doubtful how much significance can be attached to attempts to obtain a complete solution of the Poisson–Boltzmann equation (7).[54] (Failure to realise these fundamental difficulties had previously led to discrepancies between different methods of deriving the electrical free energy of the solution from the average potential of an ion.)[55] The error involved in such elaborations can only be estimated by an extension of Kramers's statistical treatment to more concentrated solutions: this involves great mathematical difficulties, and has not yet been attempted. It may be mentioned that Bjerrum's theory of ion association[56] is probably less open to such criticism, since he does not apply the Poisson–Boltzmann equation to pairs of ions close together, which is just when the usual assumptions are least valid.

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[49] *Trans. Faraday Soc.*, 1927, **23**, 434; *A.*, 1927, 1028. L. Onsager (*Chem. Reviews*, 1933, **13**, 73) has recently shown that Fowler's "fluctuation terms" are not actually negligible, but are cancelled out by another term omitted by Fowler.

[50] *Physikal. Z.*, 1927, **28**, 277; *A.*, 1927, 157.

[51] *Proc. K. Akad. Wetensch. Amsterdam*, 1927, **30**, 145; *A.*, 1927, 626. The same conclusion is arrived at by P. van Rysselberghe, *J. Chem. Physics*, 1933, **1**, 205.

[52] See, further, G. Scatchard, *Physikal. Z.*, 1932, **33**, 22; *A.*, 1932, 127; Scatchard and J. G. Kirkwood, *ibid.*, p. 297; *A.*, 1932, 467.

[53] For an excellent account of these difficulties, see L. Onsager, ref. (49).

[54] Such attempts are dealt with in *Ann. Reports*, 1932, **29**, 24. The complete solution of the Poisson–Boltzmann equation has also been obtained for unsymmetrical electrolytes, see V. K. LaMer, T. H. Gronwall, and L. J. Greiff, *J. Physical Chem.*, 1931, **35**, 2245; *A.*, 1931, 1127.

The Debye–Hückel limiting law (which is unaffected by the above considerations) is readily applicable to mixtures of electrolytes; for the activity coefficient of the salt AB in any dilute electrolyte mixture it gives the expression

$$\log f_{AB} = -\alpha z_A z_B \sqrt{\mu} \quad . \quad . \quad . \quad . \quad . \quad (9)$$

where z_A and z_B are the valencies of the ions A and B, and μ is defined by $\mu = \frac{1}{2}\sum\limits_i z_i \gamma_i^2$, the summation being extended over all ions present in the solution; α is a constant depending on the temperature and the dielectric constant of the medium. Since in the presence of solid salt the chemical potential of AB is constant, determinations of the solubility of salts in presence of other electrolytes constitute a simple experimental test of equation (9), and the first reliable evidence for the Debye–Hückel theory was obtained in this way.[57] Later work has in many cases led to confirmation of the theory both in aqueous[58] and in non-aqueous[59] solvents.

The experimental results appear in some cases to be at variance with equation (9) even at very great dilutions, notably for salts of unsymmetrical higher-valency types[60] and solvents of low dielectric constant.[61] It is, however, just in these cases that approximations (*a*), (*b*), and (*c*), above, break down outside an extremely small concentration range, and it can, in fact, be shown that the range in which the limiting law will be obeyed is in many cases too dilute to be studied experimentally. We shall not deal further here with attempts to explain the behaviour of electrolytes outside this range. As mentioned above, considerable uncertainty attends any more elaborate solution of equation (7), and the evidence for and against assuming incomplete dissociation (in any sense) has been recently dealt with in these reports.[62] It may, however, be mentioned that solubility data in aqueous and in non-aqueous solution have been interpreted successfully both by the Gronwall–LaMer–Sandved extended theory [63] and by assuming incomplete dissociation.[64]

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[55] See L. Onsager, *loc. cit.*, ref. (53).

[56] See *Ann. Reports*, 1932, **29**, 32.

[57] *Ann. Reports*, 1925, **22**, 32.

[58] See V. K. LaMer, C. V. King, and C. F. Mason, *J. Amer. Chem. Soc.*, 1927, **49**, 363; *A.*, 1927, 314 (cobaltammines); S. Popov and E. W. Neuman, *J. Physical Chem.*, 1930, **34**, 1853; *A.*, 1930, 1107 (silver chloride); B. H. Peterson and E. L. Meyers, *J. Amer. Chem. Soc.*, 1930, **52**, 4853; *A.*, 1931, 309 (cupric iodate); E. Larsson and B. Adell, *Z. anorg. Chem.*, 1931, **196**, 344; *A.* 1931, 566 (silver benzoate and acetate).

[59] A. L. Robinson, *J. Physical Chem.*, 1928, **32**, 1089; *A.*, 1928, 944 (potassium bromide in acetone); J. W. Williams, *J. Amer. Chem. Soc.*, 1929, **51**, 1112; *A.*, 1929, 649 (cobaltammines in methyl alcohol); L. A. Hansen and J. W. Williams, *ibid.*, 1930, **52**, 2759; *A.*, 1930, 1121 (cobaltammines in ethyl alcohol–water mixtures); J. N. Brönsted, *loc. cit.*, ref. (18).

[60] V. K. LaMer, C. V. King, and C. F. Mason, *J. Amer. Chem. Soc.*, 1927, **49** 410; *A.*, 1927, 314; LaMer and F. H. Goldman, *ibid.*, 1929, **51**, 2632; *A.* 1929, 1386.

A principle of very general application in correlating activity coefficients in mixtures of electrolytes is the "principle of specific interaction," first stated by J. N. Brönsted [65] and recently derived in a more lucid manner by E. A. Guggenheim.[66] If we consider a salt AB present in very small amount in a solution of a salt XY, then the activity coefficient of AB (written $f_{AB(XY)}$) depends essentially upon the interactions between A and X, A and Y, B and X, and B and Y. The principle of specific interaction assumes that these interactions are determined entirely by the electric charges when the two ions are of the same sign, but that when the two ions are of opposite signs, specific effects (*e.g.*, the radii of the ions, short range forces, etc.) will be of importance. This obviously depends upon the fact that similarly charged ions are very rarely close to one another, while oppositely charged ions tend to spend an appreciable time in close proximity. Many of the observed deviations from the Debye–Hückel theory may be explained in this way. For instance, LaMer, King, and Mason [67] found that although the solubility of the salt $[\mathrm{Co(NH_3)_6}]^{\cdot\cdot\cdot}[\mathrm{Co(NH_3)_2(NO_2)_2C_2O_4}]_3'$ obeys the Debye–Hückel limiting law in solutions of potassium nitrate and barium chloride, yet there are large deviations in potassium or magnesium sulphate and potassium ferricyanide, *i.e.*, when the two multiply charged ions present are of opposite sign. The theory also leads to the following quantitative predictions :

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[61] C. A. Kraus and R. P. Seward, *J. Physical Chem.*, 1928, **32**, 1294; *A.*, 1928, 1182; J. W. Williams, *Chem. Reviews*, 1931, **8**, 303.

[62] *Ann. Reports*, 1932, **29**, 21—29.

[63] R. P. Seward and W. C. Schumb, *J. Amer. Chem. Soc.*, 1930, **52**, 3962; *A.*, 1930, 1512; Seward and C. H. Hamblet, *ibid.*, 1932, **54**, 554; *A.*, 1932, 339; A. W. Scholl, A. W. Hutchison, and G. C. Chandlee, *ibid.*, 1933, **55**, 3081; *A.*, 1014; E. W. Neuman, *ibid.*, 1932, **54**, 2195; *A.*, 1932, 801; *ibid.*, 1933, **55**, 879; *A.*, 456; LaMer, Gronwall, and Greiff, *loc. cit.*, ref. (54).

[64] H. E. Blayden and C. W. Davies, *J.*, 1930, 949; C. W. Davies, *ibid.*, p. 2410; *A.*, 1930, 860; 1931, 40.

[65] *J. Amer. Chem. Soc.*, 1922, **44**, 877; *A.*, 1922, ii, 481.

[66] Report of the 18th Scandinavian Naturalist Congress, Copenhagen, 1929

[67] *Loc. cit.*, ref. (60).

(*a*) For two solute salts AB and A′B with a common anion B, the ratio $f_{AB(XY)}/f_{A'B(XY)}$ is independent of the nature of both B and X.

(*b*) Similarly, for two solvent salts XY and X′Y, the ratio $f_{AB(XY)}/f_{AB(X'Y)}$ is independent of both A and Y.

(*c*) For a salt AB present in small amount in a mixture of x parts of XY and $1 - x$ parts of X′Y′ (the total salt concentration being constant), $\log f_{AB}$ is a linear function of x. This rule was first advanced independently by Brönsted,[65] but its relation to the specific interaction principle was later shown by E. Güntelberg [68] and by Guggenheim.[69]

These predictions (in which, of course, the rôles of anion and cation are interchangeable) were shown by Brönsted to be in accordance with a large mass of data for the solubility of cobaltammines in salt solutions up to 0·1*N*. Subsequent solubility measurements by LaMer and his collaborators [70] have further confirmed the principle, and extended it to include salts of higher valency types. Only for cadmium chloride [71] does the principle fail, probably owing to the formation of complex ions.

The prediction of the thermodynamic properties of non-electrolyte mixtures over the whole concentration range must be regarded as one of the most difficult problems in the theory of solutions. In spite of a great deal of theoretical and experimental work, little real progress has been made since the matter was last dealt with in these reports.[72] The subject is still generally treated from the point of view of deviations from the perfect solution, which is best defined by the equation

$$\bar{F}_i - \bar{F}_i^0 = RT \log N_i \quad . \quad . \quad . \quad . \quad (10)$$

where N_i is the mole fraction, and $\bar{F}_i^0$ refers to pure component (and not to the dilute solution). There seems, however, to be a growing suspicion that equation (10) may not represent in any sense a " normal " behaviour of a liquid mixture, but may rather be due to an unusual and complex compensation of several effects. It is well known that if equation (10) is true for a binary mixture over a certain temperature range, then the two components will mix without energy or volume change over the same temperature range. E. A. Guggenheim[73] has pointed out that the converse of this proposition is not in general true, and has shown that equation (10) can only be deduced by making much more drastic assumptions about the energy and volume relations. He has also attempted to derive the same equation by statistical methods,[74] but his treatment would only appear to be valid for the whole concentration range when the two components have equal molecular volumes, and the same applies to W. Heitler's treatment of the liquid as a cubic lattice.[75]

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[68] E. Güntelberg, *Z. physikal. Chem.*, 1926, **123**, 199; *A.*, 1926, 1207.

[69] E. A. Guggenheim, *loc. cit.*, ref. (66).

[70] LaMer, King, and Mason; LaMer and Goldman, *locc. cit.*, ref. (60); LaMer and R. G. Cook, *J. Amer. Chem. Soc.*, 1929, **51**, 2622; *A.*, 1929, 1386.

[71] H. B. Friedman and V. K. LaMer, *ibid.*, 1931, **53**, 103; *A.*, 1931, 309.

[72] *Ann. Reports*, 1925, **22**, 37.

In attempting to account for deviations from the laws of perfect solution, it is certainly necessary at present to consider only solutions in which the constituents are as far as possible non-polar, and the molecular attractions are essentially due to the van der Waals forces. For such systems J. H. Hildebrand[76] has proposed the equation

$$\bar{F}_2 - \bar{F}_2^0 = RT \log N_2 + \beta N_1^2 \quad . \quad . \quad . \quad (11)$$

where β is a constant for a given mixture and temperature. This equation is in good agreement with the experimental data for solubilities and vapour pressures in a large number of solutions, which Hildebrand terms "regular solutions." He suggests that such solutions are characterised by an absence of chemical and orienting effects, and that the entropy of mixing is the same as for a perfect solution of the same concentration. The last assumption is by no means self-evident unless the molecules are quite symmetrical, but it (or its equivalent) is made in every theory of deviations from perfection. It then follows immediately that the term βN_1^2 should represent $\bar{H}_2$, *i.e.*, the partial molal heat of mixing of component 2; this is in agreement with the experimental data in some cases, especially when the components are non-polar.[77] J. J. van Laar and R. Lorenz[78] have derived equation (11) on the basis of the van der Waals equation of state; this, however, leads to a value of β independent of temperature, which is not in accordance with experiment. W. Heitler[79] has arrived at the same equation by treating the structure of the liquid as a cubic lattice, but his deduction only applies to the case of equal molecular volumes. No entirely satisfactory derivation of equation (11) has been given; moreover, since the term expressing deviations from ideality must depend on the forces between the molecules, we should expect it to be a function of the volume of the solution. Any exact treatment of the problem is exceedingly difficult owing to lack of knowledge of the spatial distribution of the molecules in liquids. Our only real knowledge of this last problem is derived from X-ray studies,[80] and Hildebrand and S. E. Wood[81] have recently made a very interesting attempt to apply the results of H. Menke[82] on the structure of mercury to calculate the thermodynamic properties of binary mixtures of symmetrical molecules. The deduction involves several approximations, but is noteworthy as the first attempt to employ our knowledge of the actual structure of liquids in this field. The final equation is

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[73] *J. Physical Chem.*, 1930, **34**, 1751; *A.*, 1930, 1120.

[74] *Proc. Roy. Soc.*, 1932, **135**, [*A*], 181; *A.*, 1932, 338.

[75] *Ann. Physik*, 1926, **80**, 630; *A.*, 1926, 1006.

[76] *J. Amer. Chem. Soc.*, 1929, **51**, 66; *A.*, 1929, 266.

[77] See *Ann. Reports*, 1925, **22**, 38.

[78] *Z. anorg. Chem.*, 1925, **145**, 239; *A.*, 1925, ii, 866.

[79] *Loc. cit.*, ref. (75); cf. J. H. Hildebrand and E. J. Salstrom, *J. Amer. Chem. Soc.*, 1932, **54**, 4257; *A.*, 26.

$$\bar{F}_2 - \bar{F}_2^0 = RT \log N_2 + A_{12}v_1^2 \quad . \quad . \quad . \quad (12)$$

where

$$A_{12} = V_2\{(E_2/V_2)^{\frac{1}{2}} - (E_1/V_1)^{\frac{1}{2}}\}^2$$

where v_1 is the volume fraction of component 1, E_1, E_2 are the cohesive energies, and V_1, V_2 the volumes per mol. of the pure components. Hildebrand shows that this equation agrees excellently with his data for the solubility of iodine in titanium, silicon, and carbon tetrachlorides and carbon disulphide. Exactly the same equation has been derived by G. Scatchard[83] by making a somewhat arbitrary assumption about the energy of mixing. He found that the equation agreed better than equation (11) with the form of the curves for $\bar{F}_2 - \bar{F}_2^0$, but that the actual magnitude of the deviation term was often in error. It should, however, be noted that the systems he has chosen involve less symmetrical molecules than those treated by Hildebrand. Scatchard found fair agreement for the observed and the calculated solubilities of naphthalene in a number of solvents.

If the molecular volumes are equal, equation (12) reduces to (11), and it is difficult to distinguish between them experimentally except in the case of widely different molecular volumes. The constants β and A_{12} in these equations are a measure of how far the system departs from ideal behaviour. Hildebrand has previously suggested that β should be approximately proportional to the difference in internal pressures,[84] but equation (12) suggests that the difference of the energy densities is a more reliable criterion. For a fluid obeying the van der Waals equation, the two are identical, indicating at least a qualitative truth in Hildebrand's original theory of solubility. R. P. B.

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[80] See *Ann. Reports*, 1929, **26**, 306.

[81] *J. Chem. Physics*, 1933, **1**, 817.

[82] *Physikal. Z.*, 1932, **33**, 593; *A.*, 1932, 986; cf. also O. Kratky, *ibid.*, 1933, **34**, 482; *A.*, 768.

[83] *Chem. Reviews*, 1931, **8**, 321.

[84] See *Ann. Reports*, 1925, **22**, 38; J. H. Hildebrand and M. E. Dorfman, *J. Amer. Chem. Soc.*, 1927, **49**, 729; *A.*, 1927, 405; (Miss) M. E. Dice and Hildebrand, *ibid.*, 1928, **50**, 3023; *A.*, 1929, 131; W. Westwater, H. W. Frantz, and Hildebrand, *Physical Rev.*, 1928, **31**, 135; *A.*, 1928, 228; Hildebrand and J. M. Carter, *J. Amer. Chem. Soc.*, 1932, **54**, 3592; *A.*, 1932, 1197.

2. ELECTROCHEMISTRY.

The Heavy Isotope of Hydrogen.

The hydrogen isotope of mass 2 has been the subject of a continually increasing volume of research during the year. A variety of methods of concentrating the isotope has been explored and the uncertainty as to the proportion of the isotope in ordinary hydrogen has been largely removed. A preliminary survey of the physical properties of the oxide (" heavy water ") has been carried out and a few extremely interesting observations of the chemical behaviour of the isotope have already been recorded. As the quantity available for investigation multiplies (and water containing 0·5% of the heavy isotope is already available commercially), results of the greatest chemical importance are likely to accumulate rapidly.

An isotope of such marked individuality is most conveniently treated as a new element and deserves a name of its own. Its discoverers have suggested the name " deuterium," the corresponding ion being called the " deuton "; there are, however, various difficulties connected with these names and Lord Rutherford has suggested " diplogen " for the atom and " diplon " for the ion, and it seems likely that, among British chemists at any rate, the latter nomenclature will find more favour. Fortunately both alternatives lead to the symbol " D " for the new atom.

The following processes have so far been shown to lead to an appreciable concentration by fractionation of the heavy isotope: (1) Distillation of liquid hydrogen[1] (the original method); (2) electrolysis of water in acid and in alkaline solution;[2, 3, 4] (3) adsorption of hydrogen on charcoal;[5] (4) distillation of water;[6] (5) adsorption of water on charcoal;[7] (6) reduction of water by hot iron;[8, 9] (7) diffusion of hydrogen through palladium;[10] (8) displacement of hydrogen in acids by zinc.[11]

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[1] H. C. Urey, F. G. Brickwedde, and G. M. Murphy, *Physical Rev.*, 1932, [ii], **40**, 1; *A.*, 1932, 554.

[2] E. W. Washburn and H. C. Urey, *Proc. Nat. Acad. Sci.*, 1932, **18**, 496; *A.*, 1932, 894.

[3] G. N. Lewis, *J. Amer. Chem. Soc.*, 1933, **55**, 1297; *A.*, 442.

[4] C. H. Collie, *Nature*, 1933, **132**, 568.

[5] H. S. Taylor, A. J. Gould, and W. Bleakney, *Physical Rev.*, 1933, **43**, 496.

[6] G. N. Lewis and R. E. Cornish, *J. Amer. Chem. Soc.*, 1933, **55**, 2616; *A.*, 793.

[7] E. W. Washburn and E. R. Smith, *J. Chem. Physics*, 1933, **1**, 426.

Of these methods, only the second has so far been used for the systematic concentration of large quantities of diplogen. The technique G. N. Lewis and his collaborators employed is described in a paper by him and R. T. Macdonald.[12] Their raw material was water from an old electrolytic bath containing about twice the normal concentration of the heavy isotope. A solution of approximately $M/5$-sodium hydroxide was electrolysed with nickel electrodes until the volume was reduced ten-fold; the solution was carbonated and distilled, and the process repeated. From 20 litres of original solution, Lewis obtained 1·5 c.c. of specific gravity 1·073 (corresponding to 66% D_2O), and ultimately from several series of electrolyses he prepared 1·3 c.c. of practically pure D_2O.

The electrolytic separation is not perfect, and the gas liberated at the cathode contains an appreciable proportion of diplogen. According to Lewis and Macdonald, when the amount of H_2O has been reduced by electrolysis by a factor n, the amount of D_2O is reduced by a factor n^α, where α is approximately 0·2 for electrolysis at 35°. D. H. Rank[13] has pointed out that, owing to evaporation, a rise in temperature will increase the apparent value of α with a corresponding fall in the efficiency of separation. Two important corollaries to the imperfection of the electrolytic separation are (i) that technical electrolytic baths continually replenished by water tend to reach a relatively small equilibrium concentration of D_2O, and (ii) that it is expedient in the later stages of the electrolytic concentration to recombine the mixture of hydrogen and diplogen evolved.

Not much has been done so far to investigate the conditions affecting the efficiency of the electrolytic separation, and accordingly the mechanism is still in doubt. Since it has been estimated that the difference in the reversible electrode potentials of the two ions must be small,[14] the principal alternatives seem to be: (1) The greater speed with which the lighter ion picks up an electron from the cathode to form a neutral atom; (2) the greater speed of union of hydrogen atoms on the cathode to form molecular hydrogen,

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[8] W. Bleakney and A. J. Gould, *Physical Rev.*, 1933, **44**, 265; *A.*, 994.

[9] J. Horiuti and M. Polanyi, *Nature*, 1933, **132**, 819.

[10] A. and L. Farkas, *Nature*, 1933, **132**, 892.

[11] A. and L. Farkas; communicated to the Royal Society by Professor E. K. Rideal on Dec. 16th, 1933.

[12] G. N. Lewis and R. T. Macdonald, *J. Chem. Physics*, 1933, **1**, 341.

[13] *Ibid.*, p. 750.

[14] H. C. Urey and D. Rittenberg, *ibid.*, p. 137.

compared with the rate of formation of D_2 from diplogen atoms; (3) the greater mobility of the lighter ion in solution.

J. Horiuti and M. Polanyi[15] conclude that hydrogen overvoltage is due to the inertia associated with the first of the above processes, since the rate of establishment of equilibrium between gaseous diplogen and its ions in aqueous solution at a platinum surface is very sensitive to the composition of the solution. R. P. Bell and J. H. Wolfenden,[16] who have investigated the influence of various factors on the efficiency of the electrolytic separation, also conclude that the separation in alkaline solution depends primarily on the first of the three factors enumerated above. B. Topley and H. Eyring[16a] have independently arrived at somewhat similar conclusions.

The proportion of the heavy isotope in ordinary hydrogen has been variously estimated. Some of the original estimates were undoubtedly too low because they depended on spectroscopic measurements of electrolytic hydrogen, which inevitably contains less than the ordinary amount of diplogen. G. N. Lewis and R. T. Macdonald,[12] from a pyknometric comparison of ordinary water with pure water, have suggested the proportion 1 : 6,500, but in a later communication[6] Lewis makes the (as yet un-amplified) remark that this estimate is " altogether too high." W. Bleakney and A. J. Gould[8] have examined in the mass-spectrograph a specimen of hydrogen obtained by the complete decomposition of rain water with hot iron; they estimate the proportion as 1 : 5,000. The most sensitive test for the heavy isotope is the bombardment method of M. L. E. Oliphant, B. B. Kinsey, and Lord Rutherford.[17] When lithium is bombarded by accelerated diplons, α-particles are produced whose range is 50% greater than those observed when protons are used as projectiles. This method is likely not only to lead to an independent estimate of the D : H ratio in ordinary hydrogen but also to provide a rapid and accurate method of estimating the relative value of various natural and artificial sources of water rich in the heavy isotope. Two other methods of evaluating the D : H ratio in minute quantities of material have been described; E. S. Gilfillan and M. Polanyi[18] have devised a flotation method applicable to specimens of water less than 0·01 c.c. in volume; A. and L. Farkas[19] have applied the thermal conductivity method, devised for the analysis of mixtures of ortho- and para-hydrogen, to determine the isotopic ratio in diplogen–hydrogen mixtures occupying as little as 0·002 c.c. at *N.T.P.*

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[15] *Nature*, 1933, **132**, 931.

[16] *Ibid.*, 1934, **133**, 25.

[16a] *J. Amer. Chem. Soc.*, 1933, **55**, 5058.

[17] *Proc. Roy. Soc.*, 1933, [*A*], **141**, 722; *A.*, 1100; cf. G. N. Lewis, M. S. Livingston, and E. O. Lawrence, *Physical Rev.*, 1933, **44**, 55.

[18] *Z. physikal. Chem.*, 1933, **166**, [*A*], 255.

[19] *Nature*, 1933, **132**, 892.

The physical properties of pure D_2O have been examined by G. N. Lewis and R. T. Macdonald[20] and by P. W. Selwood and A. A. Frost.[21] The principal results so far obtained are summarised in the following table :

	D_2O.	Ordinary H_2O.
Melting point	3·8°	0°
Boiling point	101·42°	100°
Specific gravity at 25°	1·1056	1·0
Temperature of maximum density	11·6°	4°
Viscosity at 20° (millipoises)	14·2;[21] 12·60[22]	10·87
Surface tension at 20° (dynes/cm.)	67·8	72·75
Refractive index ($n_D^{20°}$)	1·3281	1·33293
,, ,, ($n_C^{20°}$)	1·3265	1·33094
Molar susceptibility (× 10^6)	– 13	– 13

In addition, the ratio of the dielectric constant of D_2O at infinite wave-length to that of H_2O is estimated by Lewis[23] and his co-workers as 0·990 at 25° ; the vapour-pressure ratio D_2O/H_2O rises steadily from 0·87 at 20° to 0·949 at 100°.[20] The solubilities of sodium chloride and of barium chloride in pure D_2O are of the order of 15% less than in ordinary water.[24]

Lewis and T. C. Doody[25] have measured the mobility of the ions of the heavy isotope, of chlorine, and of potassium in pure D_2O. Their results at 18° are as follows :

	$H^{\cdot}$.	$D^{\cdot}$.	$K^{\cdot}$.	Cl'.
In D_2O	—	213·7	54·5	55·3
In H_2O	315·2	—	64·2	65·2

In spite of the present discrepancy in the values for the viscosity of D_2O, it seems probable that the mobility of $D^{\cdot}$ in D_2O, when corrected for the increased viscosity of the solvent, is not more than 30% less than that of $H^{\cdot}$ in H_2O, in contrast to the predictions of Bernal and Fowler.* The measurements of Lewis and Doody do not, however, definitely exclude the possibility that mobility differences play a part in the electrolytic separation, at least in acid solution, since this may depend on the experimentally inaccessible mobility of $D^{\cdot}$ in H_2O.

The chemical behaviour of the heavy isotope has been discussed theoretically in several papers. Chemical differences between hydrogen and diplogen are to be expected on theoretical grounds for several reasons, but the dominating factor is likely to be the smaller half-quantum of zero-point energy possessed by diplogen in virtue of its greater mass. Except in the special case where the energy levels in the activated complex are displaced by a compensating amount, the lower zero-point energy will lead to a higher heat of activation for reactions involving diplogen and therefore to a lower reaction velocity. E. Cremer and M. Polanyi[26] and H. Eyring and A. Sherman[27] both anticipate that the velocity of reaction (and velocity of desorption) will be substantially smaller for the heavy isotope. H. C. Urey and D. Rittenberg[14] have calculated the free energy of the molecules D_2, DH, DCl, and DI, and thence the equilibrium constants for reactions involving these molecules and their hydrogen analogues. They estimate that the equilibrium constant $[HD]^2/[H_2][D_2]$ will fall away substantially from the value of 4 (to be expected on a random pairing-off of the two kinds of atom) as low temperatures are reached. They also conclude that the ratio of the equilibrium constants (K_1/K_2) for the two parallel reactions :

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[20] *J. Amer. Chem. Soc.*, 1933, **55**, 3057; *A.*, 894.

[21] *Ibid.*, p. 4335; *A.*, 1233.

[22] G. N. Lewis and R. T. Macdonald, *ibid.*, p. 4730.

[23] G. N. Lewis, A. R. Olson, and W. Maroney, *ibid.*, p. 4371.

[24] H. S. Taylor, E. R. Caley, and H. Eyring, *ibid.*, p. 4334; *A.*, 1240.

[25] *Ibid.*, p. 3509.

* See p. 34.

$$H_2 + I_2 = 2HI \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$
$$D_2 + I_2 = 2DI \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

will not be unity but 1·234 at 575° K. and 1·222 at 700° K. The corresponding ratio for the two parallel reactions with chlorine is estimated at 0·807 at 575° K. and 0·874 at 700° K. They further conclude, more tentatively, that the free-energy difference between the two isotopes is not likely to lead to a difference in reversible electrode potential adequate to account for the electrolytic separation.

Experimental observations of the chemical behaviour of diplogen are so far scanty but of the greatest interest. K. F. Bonhoeffer and G. W. Brown[28] have shown that, if ammonium chloride is dissolved in D-rich water, the D : H ratio in the salt after recovery approximates to that in the water; similar observations were made by Lewis in the case of ammonia.[29] Bonhoeffer and Brown found that if the same experiment is performed with sugar in D-rich water, the equipartition of D between water and sugar extends to only *half* the hydrogen atoms in the sugar so that exchange can presumably only take place with the hydroxylic hydrogen.

[26] *Z. physikal. Chem.*, 1932, [*B*], **19**, 443; *A.*, 235.
[27] *J. Chem. Physics*, 1933, **1**, 435.
[28] *Z. physikal. Chem.*, 1933, [*B*], **23**, 171; *A.*, 1242.
[29] *J. Amer. Chem. Soc.*, 1933, **55**, 3502; *A.*, 1020.

A. and L. Farkas[19] have studied the equilibrium $H_2 + D_2 = 2HD$ as set up in contact with a hot nickel wire; they find the equilibrium constant $[HD]^2/[H_2][D_2]$ to have a value of about 3 above room temperature, in accordance with the predictions of Urey and Rittenberg,[14] and to be independent of temperature in this temperature range, pointing to a negligible heat of reaction. They have also investigated the same equilibrium as established in the homogeneous gas phase above 600°.

A more unexpected observation is that of M. L. Oliphant,[30] who found that hydrogen gas rich in diplogen lost more than 95% of its diplogen content after storage over ordinary water for six weeks. Since the volume of gas was unchanged, this points to exchange between gaseous diplogen and the combined hydrogen of the water. J. Horiuti and M. Polanyi[9] have since shown that the same change proceeds more rapidly in the presence of catalytically active platinum; they suggest that the platinum assists the formation and discharge of diplogen ions as it does at a hydrogen electrode. In further experiments[15] they have shown that the rate of exchange is very sensitive to the composition of the solution, being highest in pure water and almost negligible in a mixture of alcohol (98%), water (2%) and $N/4$-potassium hydroxide; this leads Horiuti and Polanyi to conclude that the slow process determining the rate of exchange is the discharge of the ion and not the union of atoms to form molecules, a conclusion of significance for the general theory of overvoltage.

Differences between the rate of reaction of diplogen and of hydrogen in corresponding reactions have now been definitely established, and instances are likely to multiply rapidly. W. Bleakney and A. J. Gould,[8] when decomposing rain water by passage over hot iron, found that the first fraction of hydrogen, examined in the mass-spectrograph, showed a D : H ratio of 1 : 6,000 whereas the last fraction showed a ratio of 1 : 4,500. This has been confirmed by Horiuti and Polanyi.[9] A. and L. Farkas[11] have found that, if acidified water containing 50% of diplogen is treated with zinc, the residual solution contains a greatly increased proportion of the heavy isotope. E. Pacsu[31] has shown that the mutarotation of α-glucose dissolved in water containing about 50% of diplogen is only about half as rapid as the corresponding reaction taking place in ordinary water. On the other hand, E. Cremer and M. Polanyi[26] were unable to find any increased concentration of diplogen in the residual hydrogen remaining from the catalytic hydrogenation of styrol on palladium. They concluded from their experiments that hydrogen does not react more than 2·5 times as fast as diplogen with styrol under the conditions of their experiment. If the reaction proceeded by the "tunnel" mechanism of M. Born and J. Franck's [32] theory of contact catalysis, a velocity ratio of the order of 10^6 might have been expected. This observation of Cremer and Polanyi is primarily of interest in so far as it foreshadows the application of diplogen to the solution of problems of general chemical interest.

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[30] *Nature*, 1933, **132**, 765; *A.*, 1223.

[31] *J. Amer. Chem. Soc.*, 1933, **55**, 5056.

Mention must be made of the biological behaviour of heavy water. Lewis [33] has shown that tobacco seeds will not germinate in nearly pure D_2O and only grow half as fast in 50% D_2O as in pure water. H. S. Taylor and his collaborators [34] have shown that pure D_2O kills a variety of small organisms with a speed roughly proportional to the degree of organisation of the animal: for instance, tadpoles are killed in one hour, protozoa in 48 hours; 30% D_2O seemed to be without effect on the organisms studied.

Our knowledge of the chemistry of diplogen is still extremely slender, but the possibilities of future development are innumerable. Apart from the interest attaching to the individual behaviour of a new atom of such general chemical importance, it is highly probable that diplogen and its compounds will prove a versatile weapon in attacking many problems of general interest. The behaviour of D_2 in gas reactions and the catalytic activity of the diplon in solution are only two out of many possible directions in which experiments with the new atom may prove illuminating in physical chemistry. In organic chemistry the new possibilities of isomerism are almost inexhaustible; the new isotope is likely to prove even more valuable in affording a new approach to many problems of structure and reaction mechanism (such as those involving hydrogen migration) by a method somewhat akin to that of radioactive indicators.

The possibilities of the diplon in effecting artificial disintegration are discussed in the report on Radioactivity and Sub-atomic Phenomena.

A Theory of the Structure of Water and Ionic Solutions.

A recent paper by J. D. Bernal and R. H. Fowler [35] describes an unusual approach to a variety of problems of considerable physicochemical interest. Not only does it suggest a "pseudocrystalline" structure for liquid water, but it applies the postulated structure to account qualitatively and sometimes quantitatively for phenomena as apparently unrelated as the heat of sublimation of ice, the variation of dielectric constant of water with temperature, the degree of hydration of ions and their heats of hydration, the viscosity of electrolytic solutions, and the abnormal mobilities of hydrogen and hydroxyl ions in water.

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[32] *Nach. Ges. Wiss. Göttingen,* 1930, 77; *A.*, 1931, 318.

[33] *J. Amer. Chem. Soc.*, 1933, **55**, 3503; *A.*, 1093.

[34] H. S. Taylor, W. W. Swingle, H. Eyring, and A. H. Frost, *J. Chem. Physics*, 1933, **1**, 751.

[35] *J. Chem. Physics*, 1933, **1**, 515. A shortened form of the paper is given in *Trans. Faraday Soc.*, 1933, **29**, 1049; *A.*, 1106.

From the density of water, which is much less than would be expected for a close-packed liquid with the known molecular dimensions of water, and from the *X*-ray diffraction curves of liquid water, Bernal and Fowler infer that the molecules are for the most part arranged in a four-co-ordinated structure similar to the distribution of SiO_2 molecules in quartz. Such an arrangement ("Water-II") predominates in the liquid between 0° and 100°; supercooled water contains a certain proportion of a tridymite-like arrangement of molecules ("Water-I") corresponding to the structure of ice itself; above 100°, and to an increasing extent as the critical point is approached, water passes over into the close-packed form ("Water-III") characteristic of an ideal liquid. The tetrahedral co-ordination of both Water-I and Water-II harmonises with the wave-functions of the water molecule, which lead to a picture of electrical-density distribution resembling a tetrahedron with two corners of positive charge and two of negative charge. The "pseudocrystalline" structure of both forms differs from that of a true crystal in the irregularity of the co-ordination and the continual fluctuations of the arrangement.

Among the manifold applications of this picture of water, those relating to ionic solutions are of the greatest interest to chemists. The hydration of an ion will occur when the potential energy of a water molecule co-ordinated with the ion (in the crystallographic sense) is less than that of the molecule in free water, where it is co-ordinated with other water molecules. Both potential energies are calculated in terms of simple Coulomb forces from the model of the water molecule inferred from spectroscopic and dipole data and from the radius and charge of the ion. On this basis it is shown that all univalent ions whose radius is less than 1·6 Å. and all polyvalent monatomic ions must be hydrated. If it is assumed that those ions are hydrated whose apparent volume in solution is much less than their volume in the solid state, the above conclusion is in harmony with the facts.

In calculating heats of hydration, it is assumed that each ion is surrounded by a sphere of co-ordinated water molecules outside which the water behaves as a continuous dielectric. The heat developed in the formation of the co-ordination sphere is calculated in terms of the mutual potential energy of ion and dipole as indicated above; that developed in the dielectric is calculated by the well-known Born formula for the work of electrostatic solvation, the radius of the co-ordination sphere being used instead of that of the ion. A number of complicating factors, such as the mutual influence of the co-ordinated water molecules on one another, makes it impossible to calculate heats of solvation in this way on purely *a priori* grounds, but Bernal and Fowler have shown that the experimental data lead to plausible values for the size of the co-ordination sphere. Their calculation thus accounts for heats of hydration in purely electrostatic terms without ignoring, like the Born–Bjerrum equation, the molecular structure of the solvent.

The application of the Bernal–Fowler model to the viscosity of electrolytes is still in a tentative and qualitative stage. It is supposed that, in addition to the simple electrostatic effect due to their charges[36] and the Brownian effect, the addition of ions to water may change its viscosity by " loosening or tightening the structure " of the liquid. Ions such as potassium or rubidium, which produce " negative viscosity " and a strong lowering of the temperature of maximum density, are regarded as being particularly effective in breaking down the structure of water. Since such an ion produces the same effect on the structure of water as a rise in temperature, it is said to raise the " structural temperature," which is defined as that temperature at which pure water would have effectively the same inner structure.

The final application of the structure of water made by Bernal and Fowler is to the abnormal mobilities of the hydrogen and the hydroxyl ion. The Grotthuss mechanism first advanced by E. Hückel[37] is developed along quantum-mechanical lines. With plausible assumptions concerning the height of the potential barriers involved, it is possible to account for the abnormal mobility of the two ions by means of a succession of jumps of protons from water molecule to water molecule or from one hydroxyl ion to another. The authors anticipate that the increased mass of the diplon ($D^{\cdot}$) will diminish the probability of the quantum-mechanical jump so greatly as to wipe out almost completely the extra mobility of $D^{\cdot}$ in D_2O. The mobility of the diplon in D_2O should therefore be about one-fifth of that of the hydrion in ordinary water. This expectation has not been realised.*

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[36] See H. Falkenhagen and M. Dole, *Z. physikal. Chem.*, 1929, [*B*], **6**, 159; *A.*, **1930**, 155.

[37] *Z. Elektrochem.*, 1928, **34**, 546; *A.*, 1929, 143.

* See p. 31.

The Mechanism of the Hydrogen and Oxygen Electrode Processes.

It is only within the last few years that progress has been made towards the elucidation of the detailed mechanism of electrode processes. On the one hand, the nature of the electrical double layer and the phenomena of electro-capillarity are being extensively investigated,[38] and on the other hand, by kinetic studies of the establishment and decay of electrode potentials, notably by F. P. Bowden [39] and by J. A. V. Butler,[40] some insight is being gained into the successive stages involved in the discharge of ions during electrolysis.*

In the latter work interest centres largely round the problem of hydrogen and oxygen over-voltages and, although the phenomena are often very complicated and their interpretation controversial, one conclusion at least seems to be emerging. It is that, in most circumstances, the rate-controlling factor which determines the over-voltage is the neutralisation of the ion and not the further stages whereby the discharged ion is transformed into the gaseous product of electrolysis. In the case of hydrogen over-voltage the crucial step is $H^{\cdot} + \varepsilon \longrightarrow H$ and not $H + H \longrightarrow H_2$. Over-voltage is thus due, not to the accumulation of atomic hydrogen, but to the slowness with which the hydrogen ions pick up electrons from the cathode. This postulate is common to the over-voltage theories both of T. Erdey-Grúz and M. Volmer [41] and of R. W. Gurney; [42] Gurney is, however, more specific as to the nature of the energy barrier between ion and metal which determines the rate of neutralisation of the ions.

Recent work suggests that at very small over-voltages at a platinum cathode complicating factors are present. G. Armstrong and J. A. V. Butler [43] have measured the rate of decay of hydrogen over-voltages at mercury and platinum cathodes. Although the results for mercury were consistent with the Gurney theory, yet the rate of decay at platinum, where the over-voltage is much smaller, was less than if it were governed solely by the transfer of electrons from the metal to the solution, and the authors conclude that in these circumstances there was an appreciable accumulation of electromotively active hydrogen at the electrode. Somewhat similarly, L. P. Hammett[44] concludes from his current–over-voltage curves for hydrogen at platinum electrodes that at high over-voltages the rate of hydrogen evolution is determined by the rate of neutralisation of the ions, but that, as the over-voltage diminishes, the rate of combination of hydrogen atoms becomes the dominant factor.

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[38] See, *e.g.*, O. Stern, *Z. Elektrochem.*, 1924, **30**, 508; K. Bennewitz and J. Schulz, *Z. physikal. Chem.*, 1926, **124**, [*A*], 115; *A.*, 1926, 1212; A. Frumkin, *Ergeb. exakt. Naturwiss.*, 1928, **7**, 240; F. O. Koenig, *Z. physikal. Chem.*, 1931, **154**, [*A*], 421, 454; *A.*, 1931, 801; J. Philpot, *Phil. Mag.*, 1932, **13**, 775; *A.*, 1932, 470; S. R. Craxford, *ibid.*, 1933, **16**, 849.

[39] *Proc. Roy. Soc.*, 1929, [*A*], **125**, 446; *A.*, 1929, 1391; *ibid.*, **126**, 107; *A.*, 1930, 169.

[40] *Trans. Faraday Soc.*, 1924, **19**, 734; *A.*, 1924, ii, 598; *ibid.*, 1932, **28**, 379; *A.*, 1932, 700; *Proc. Roy. Soc.*, 1932, **137**, [*A*], 604; *A.*, 1932, 1092.

[41] *Z. physikal. Chem.*, 1930, **150**, [*A*], 203; *A.*, 1930, 1376.

[42] *Proc. Roy. Soc.*, 1931, [*A*], **134**, 137; *A.*, 1931, 25; cf. *Ann. Reports*, 1932, **29**, 34.

[43] *Trans. Faraday Soc.*, 1933, **29**, 1261.

* A paper by A. Frumkin (*Z. physikal. Chem.*, 1933, **164**, [*A*], 121; *A.*, 468) makes some progress towards correlating these two fields of investigation.

It is well known that the " oxygen electrode " does not behave in a thermodynamically reversible manner, the *E.M.F.* of the hydrogen–oxygen cell being far from reproducible and falling short of the theoretical value by about 0·2 volt. This is generally attributed to the presence of oxides of platinum, which prevents the saturation of the electrode with oxygen. Support for this view and a further insight into the mechanism of the oxygen electrode are afforded by a recent paper by T. P. Hoar,[45] according to whom a platinum electrode in oxygen-saturated electrolyte is covered by an oxide film containing cracks and pores. The abnormally low potential of the electrode is due to a continuous flow of current between the film and the relatively anodic metal, causing an irreversible removal of electromotively active material from the film. If, however, the current necessary for this irreversible oxide formation is supplied by a cathode other than the film itself, *i.e.*, if the electrode is anodically polarised by an external source of current, the reversible potential may be obtained. Hoar measured the current necessary to keep a bright platinum electrode in oxygen-saturated electrolyte at its theoretical reversible potential by anodic polarisation. This current falls off at first rapidly with time and then slowly at a rate quantitatively consistent with the hypothesis that a progressive closing-up of the pores in an oxide film is taking place.

Cathodic and anodic polarisation curves were then measured at considerably higher current densities, where the irreversible process would be relatively insignificant. In both cases the logarithm of the current density varied linearly with the voltage except at very low current densities. By extrapolating both anodic and cathodic curves back to the potential at which the rates of charge and discharge of ions would be equal, the reversible potential of the oxygen electrode was found to be 1·20, in fair agreement with the theoretical value.

J. H. W.

[44] *Trans. Faraday Soc.*, 1933, **29**, 770. [45] *Proc. Roy. Soc.*, 1933, [*A*], **142**, 628.

3. CHEMICAL KINETICS.

In this section some special problems have been selected for discussion.

Energy Transfer Relations.

It is in connexion with problems of energy transfer that reaction kinetics comes into closest relation with theoretical physics on the one hand and with experimental spectroscopy on the other. From the chemical point of view the specificity of such changes is well recognised, and there are now innumerable examples of their importance in molecular activation and deactivation.

An interesting physical method of approaching the problem is by the study of the variation of the velocity of sound with frequency.[1] At very high frequencies the adiabatic changes accompanying the passage of sound through a gas are too rapid to allow the establishment of equilibrium between the translational and vibrational energy of the molecules : thus the effective value of γ will change at frequencies where the failure of complete energy equilibrium sets in. A. Eucken and R. Becker [2] have studied the dispersion of sound in carbon dioxide and in chlorine, in the absence and in the presence of foreign gases. The latter help to maintain the equilibrium between translational and vibrational energy, but vary very much in effectiveness. Hydrogen, hydrogen chloride, and methane were found to be effective, while argon was ineffective. The contrast between hydrogen and argon recalls the relative efficiency of these two gases in maintaining the rates of unimolecular reactions at low pressures.

In discussing the theoretical aspect of the matter, Franck and Eucken express the view that the important factor in energy transfers is the extent to which the linking of the molecule receiving the vibrational energy is modified by the proximity of the second colliding molecule. In other words, there must be mutual disturbance of the potential curves. Molecules can be set in vibration by the impact of electrons, because the electrons penetrate the molecules and cause such a disturbance of the bindings that the nuclei find themselves with a mutual potential energy and begin to vibrate. The inefficacy of helium in communicating energy in unimolecular reactions is attributed to the fact that it will be repelled by saturated molecules; the diatomic hydrogen is not similarly repelled because its own potential-energy curve can suffer modification as it approaches. Particularly great disturbances by exchange forces are to be expected when radicals or free reactive atoms approach a molecule, and dipoles and ions should favour transfers because of the disturbance which they create in the electronic system.

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[1] J. Franck and A. Eucken, *Z. physikal. Chem.*, 1933, [*B*], **20**, 460, where references to the work of Pierce; Kneser; Herzfeld and Rice; Richards and Reid; Eucken, Mücke, and Becker; and Henry are given.

[2] *Z. physikal. Chem.*, 1933, [*B*], **20**, 467; *A.*, 554.

In this connexion, the efficiency of free atoms of halogens in catalysing the decomposition of nitrous oxide may be recalled.[3] The decomposition of various organic substances possessing a mobile hydrogen and a breakable C–C linkage is strongly catalysed by the highly polarisable molecule of iodine, and it is significant that all the substances whose reactions are promoted in this way possess dipole moments in or near the bond broken in the chemical change.[4] The influence of ion pairs in catalysing the isomeric change of oximes is also noteworthy.[4a]

According to the theoretical considerations of O. K. Rice,[5] probability of energy transfer decreases with increasing mass of the colliding particle. In the decomposition of nitrous oxide, the relative probability of activation by collision of nitrous oxide molecules with molecules of the rare gases appears to decrease from helium to xenon.[6]

If internal rearrangements of energy are difficult, it is possible to conceive the existence of different kinds of activated state. When the molecule has received energy in a collision, and this energy is located in the molecule in a particular way, there may be one probability of chemical decomposition, whereas when the energy is located in another way there may be another probability. If the molecule is of moderate complexity, there may be, quite apart from continuous variations of transformation probability with total energy, a limited number of activated states which can be regarded as qualitatively different. If this is so, there will appear to take place a number of simultaneous reactions, differing in physical mechanism, but chemically identical. It can be shown that these reactions will be differently influenced by pressure. Investigation, over a wide range, of the influence of pressure on the decomposition of acetaldehyde shows that the physical mechanism of the reaction must be regarded as a composite one in the above sense.[7] The idea of a balance between activating and deactivating collisions, and the recognition of the ability of almost any type of foreign molecule to contribute to these processes in a highly specific manner, make it possible to correlate the most diverse relations between rate of reaction and concentration, and simplify the classification of chemical changes. It is now usually not profitable to attempt to specify the influence of various concentrations in terms of an " order of reaction." Instead, it is better to write down an equation expressing the rate of formation and destruction of active molecules,[8] or of an activated complex of a reactant molecule and a catalyst molecule, and solve it for the concentration of activated molecules. The rate of reaction will in general be proportional to the latter. Every substance present contributes potentially to activation and to deactivation, and according to the value of the specific constants expressing this, the most varied relations appear as special cases.[9] In this way the well-known " quasi-unimolecular " reaction which changes from the first order to the second with diminishing initial concentration is accounted for, and the influence of various foreign substances is expressed. Other special cases are catalytic reactions the rate of which is proportional to the concentration of the catalyst, catalytic reactions with a rate nearly independent of the catalyst concentration, and either of the first order with respect to the reacting substance itself, or even apparently impeded by increase in the reactant concentration. Examples of all these types are now known.

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[3] F. F. Musgrave and C. N. Hinshelwood, *Proc. Roy. Soc.*, 1932, [*A*], **137**, 25; *A.*, 1932, 917; M. Volmer and M. Bogdan, *Z. physikal. Chem.*, 1933, [*B*], **21**, 257; *A.*, 680.

[4] S. Bairstow and C. N. Hinshelwood, *Proc. Roy. Soc.*, 1933, [*A*], **142**, 77; *A.*, 1251.

[4a] T. W. J. Taylor and D. C. V. Roberts, *J.*, 1933, 1439.

[5] *J. Amer. Chem. Soc.*, 1932, **54**, 4558; *A.*, 129.

[6] M. Volmer and M. Bogdan, *loc. cit.*, ref. (3).

[7] C. J. M. Fletcher and C. N. Hinshelwood, *Proc. Roy. Soc.*, 1933, [*A*], **141**, 41; *A.*, 910.

Catalytic Actions of Magnetic Substances.

The conversion of para- into ortho-hydrogen is catalysed by magnetic molecules. In the gas phase, oxygen, nitric oxide, and nitrogen peroxide are active.[10] The reaction is bimolecular, being of the first order with respect to the para-hydrogen and having a rate proportional to the catalyst concentration. At 293° K. the velocity constants for the three catalysts are 9·16, 34·9, and 12·5 litre/mol./min. respectively. The effectiveness of the collisions in causing transformation varies little with temperature. The interconversion of para- and ortho-hydrogen is also catalysed by various solvents,[11] the velocity constants being about 5×10^{-6} times those of the gas reaction. The action of the solvent is attributed to the influence of the nuclear magnetic moment of the hydrogen atoms which it contains. The reaction is also catalysed by various paramagnetic ions, the rate being proportional to the square of the magnetic moment of the ion. Catalysis by dissolved oxygen occurs at a rate corresponding to the rate in the gas phase.

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[8] *Ann. Reports*, 1931, **28**, 41.

[9] *Proc. Roy. Soc.*, 1933, [*A*], **142**, 77; *A.*, 1251.

[10] L. Farkas and H. Sachsse, *Z. physikal. Chem.*, 1933, [*B*], **23**, 1; *A.*, 1251.

[11] *Idem*, *ibid.*, p. 19.

Interconversion of the two forms of hydrogen in contact with solid substances at low temperatures also depends upon the paramagnetism of the solid.[12]

The theory of the magnetic conversion has been given by E. Wigner.[13]

Influence of Internal Electronic Displacements on Reaction Velocity.

If there is an appreciable dipole moment located in a particular bond of a molecule, then in accordance with the sign of the moment there will be a certain displacement of electrons throughout the molecule either towards or away from the bond containing the dipole. In many chemical reactions one atom or group can be regarded as the principal seat of the change (*e.g.*, in the hydrolysis of an alkyl halide the behaviour of the halogen atom is clearly the factor of primary importance), and the drift of electrons towards or away from it may modify the reactivity profoundly. It is far from easy always to predict the sense in which the reactivity will be modified. If, for example, chlorine is being replaced by hydroxyl, the tendency of the chlorine to come away as a negative ion is increased by a drift of electrons towards the part of the molecule to which it is attached. On the other hand, the approach of an attacking hydroxyl ion is hindered. Some specific idea of the reaction mechanism may be necessary before the effect can be predicted. Nevertheless, organic reactions can be classified into two types : those which are facilitated by a displacement of electrons in the direction of the reacting atom or group (type A), and those which are facilitated by a corresponding displacement away from the reactive centre (type B).[14] The conception of an order of relative polarity of substituents has long been familiar in organic chemistry : it has lately become more precise on account of the possibility of measuring dipole moments. Thus, quantitative relations between " polarity " influences on reaction velocity and the magnitude of dipoles can be looked for.

In the reaction of a ketone $CH_3{\cdot}CO{\cdot}C_6H_4{\cdot}X$ with a halogen, the velocity is determined by the enolisation of the ketone, and is proportional to the hydrion concentration. It has therefore been concluded that this velocity represents the speed of association of protons with molecules of ketone. If the substituent X causes a drift of electrons away from itself, then the ease of addition of protons elsewhere in the molecule should be increased, and *vice versa*. In accordance with expectation, the rate of reaction decreases in the following order for various substituents (all in the *p*-position): Me, H, I, Br, Cl, NO_2. By making the assumption, not yet justified by direct experiment, that the reaction rate is connected with the energy of activation by the simplest possible relation: rate = collision number × $e^{-E/RT}$, changes in velocity from substance to substance can be recalculated as changes in energy of activation. It then appears[15] that the difference in energy of activation caused by a substituent X is nearly linearly proportional to the dipole moment of the compound C_6H_5X.

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[12] K. F. Bonhoeffer, A. Farkas, and K. W. Rummel, *Z. physikal. Chem.*, 1933, [*B*], **21**, 225; *A.*, 680; H. S. Taylor and H. Diamond, *J. Amer. Chem. Soc.*, 1933, **55**, 2613; *A.*, 788.

[13] *Z. physikal. Chem.*, 1933, [*B*], **23**, 28; *A.*, 1256.

[14] C. K. Ingold and E. Rothstein, *J.*, 1928, 1217.

In many other reactions, especially side-chain reactions of aromatic compounds, the same order of substituents is found, whether we arrange them according to decreasing velocity of reactions of type A or increasing velocity of reactions of type B. This order is CH_3, H, Halogens, NO_2. Recalculating differences in speed in terms of a hypothetical difference in energy of activation, we find a similar quantitative relation with μ, the dipole moment of C_6H_5X, *viz.*,

$$E = E_0 \pm c(\mu - a\mu^2)$$

E_0 is the heat of activation when there is no substituent in the benzene nucleus, E the corresponding value when the substituent X is present. The alternative signs apply according as the reaction is of the type A or B. When X is in the meta-position the relation applies rather exactly for all except halogen substituents; for para-substituents the deviations from a quantitative relation appear to be greater. The halogens deviate from the quantitative relation in such a way that they could be made to fit it if they were credited with larger dipole moments than the measured ones. In this connexion it is pointed out [15] that L. E. Sutton's work [16] shows the aromatic halogen compounds to have dipole moments smaller than would be expected from analogies with aliphatic halogen compounds: some factor operates to reduce the measured moment. If this factor did not operate in influencing the reaction velocity, the anomalies would be partly accounted for.

The halogens are anomalous in another respect, *viz.*, that, although as a group they come among other substituents in the order to be expected from the dipole moments, yet they are often in an inverted or in an apparently random order among themselves.[17] It is well known that to explain the facts of aromatic substitution two opposing effects of halogens in producing electron displacements have to be postulated; and the suggestion has been made that these opposing effects may operate in different ways on different parts of complex reaction mechanisms, producing a resultant which according to circumstances may be greatest for any one of the halogens. The inner mechanism of these effects, however, is still far from clear.

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[15] W. S. Nathan and H. B. Watson, *J.*, 1933, 890, 1248; *A.*, 1124.

[16] *Proc. Roy. Soc.*, 1931, [*A*], **133**, 668; *A.*, 1931, 1354.

Resonance and Stability of Molecules.

In quantum mechanics the state of a system is described by a function usually designated ψ. When the value of ψ is known, the energy of the system can in principle be calculated. If two values of ψ are possible, the state is described by the " linear combination " $a\psi_1 + b\psi_2$. This expression is, according to the rules, given the following somewhat arbitrary meaning : a and b measure the probability that a given example of the system is in the state where ψ equals ψ_1 or ψ_2 respectively. If the system under consideration is a molecule, and the two states are two conceivable electronic structures, then a and b measure the relative frequency of occurrence of these forms. A really fundamental justification of the procedure of forming linear combinations of possible proper functions is perhaps too much to expect, but it is as well to be under no misapprehension as to its essentially arbitrary nature. If ψ_1 and ψ_2 belong to two structures of nearly the same energy, and if there is the possibility that the two kinds of molecule " interact " in the sense of modifying each the potential energy of the other (a possibility which must presumably be conceded to most molecular systems), then it is found by applying Schrödinger's equation to the expression $a\psi_1 + b\psi_2$, that a and b vary with time, waxing and waning in a way which indicates a rapid oscillation of the molecules between the two possible structures. The process is called resonance. It also follows from the equations that the energy of either structure involved in the resonating process is less than it would have been had the interchange not been possible. Whatever degree of satisfaction may be felt with the logical (as distinct from the mathematical) basis of the calculation, the result can be clearly stated : when two structures of approximately equal energy are possible for a molecule, it will fluctuate between them (or, if we prefer to express it so, exist in an indefinite intermediate condition), and moreover, it will be more stable than it would have been had the alternative forms not been possible. At least this can be used as an hypothesis in attempts to interpret the facts about the stability of different types of molecule.

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[17] C. W. Shoppee, *J.*, 1933, 1117; J. W. Baker, *ibid.*, p. 1128; G. M. Bennett, *ibid.*, p. 1112; R. Robinson, *ibid.*, p. 1114; *A.*, 1151.

As an example the hydrogen halides may be considered. L. Pauling [18] estimates that the energy of hydrogen fluoride with a covalent, electron-pair link is about the same as that of the ionic molecule $\mathrm{H}^{\cdot}\mathrm{F}'$. Thus, both forms play their part: the molecule is neither covalent nor ionic, but both (the covalent form being of greater importance in this actual case). With the other hydrogen halides, the potential-energy curves of the covalent and the ionic forms do not cut, and the structure corresponds to the form of lower energy, *viz.*, the covalent form.

According to these principles, we should expect bond energies to be additive only when possibilities of resonance are absent. Energies of individual bonds, such as $\mathrm{C{-}H}$, $\mathrm{C{=}O}$, and $\mathrm{N{-}H}$, can be calculated from the heat of formation of simple compounds such as methane, ammonia, and formaldehyde. From the tabulated values, the energy of formation of a compound of any assigned electronic formula can be calculated. According to Pauling and J. Sherman,[19] if there is a considerable difference between the measured energy and the value so computed, it is to be ascribed to the " resonance energy." From an examination of a considerable number of examples, they reach the important conclusion that whenever the bond energies are not additive the deviations are in fact in the direction corresponding to greater stability of the molecule. Resonance energies varying from 0·2 to 10 volt-electrons are inferred in this way. Pauling and Sherman make the comment that the bond energy of $\mathrm{C{=}O}$ is surprisingly large, and attribute its magnitude to resonance between $\mathrm{C}::\overset{\cdot\cdot}{\mathrm{O}}:$ and $\overset{+}{\mathrm{C}}:\underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{O}}}:^{-}$. (It must be admitted, however, that the possibility of introducing semipolar links increases the possibilities of resonance in almost any kind of molecule almost indefinitely, and makes the fundamental question of a correlation between resonance forms and special stability rather more difficult to test.)

In the present connexion the aromatic compounds are of special interest, on account of the large number of possible valency arrangements in their molecules. There may be resonance between a considerable number of different structures, *e.g.*, two Kekulé and three possible Dewar structures,[20] and the resonance energy may be very great. It is suggested that this has a very important connexion with aromatic stability.

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[18] *J. Amer. Chem. Soc.*, 1932, **54**, 988.

[19] *J. Chem. Physics*, 1933, **1**, 606.

[20] L. Pauling and G. W. Wheland, *ibid.*, p. 362. For other conjugated systems, see L. Pauling and J. Sherman, *ibid.*, p. 679.

The theory has also something to say about the existence of free radicals of the triphenylmethyl type. Considering, first, hexaphenylethane, we have two carbon atoms with the normal tetrahedral disposition of valencies. These atoms are joined to one another and to three phenyl groups. If the bond joining them is broken, considerable energy is absorbed. In the two free radicals formed, a rearrangement of valencies into a coplanar structure is assumed to take place. The number of resonance possibilities is greatly increased, and the associated resonance energy is estimated to be more than enough to compensate for the rupture of the C—C link. Hence the stability of the free radical is accounted for. It is claimed that this method of treating the problem will explain many of the more special details about differences in stability of radicals differing slightly in structure.[21]

Now that the kinetics of the dissociation and recombination of such substances can be experimentally studied, as K. Ziegler [22] has shown, and energies of activation measured, there will be a wide scope for the application of theory. C. N. H.

Reactions of Free Atoms and Radicals.

Recent developments in the production of free atoms and free radicals are opening up new fields in chemistry, particularly in the preparation of new inorganic compounds and in the measurement of heats of activation of atomic reactions, these measurements being of great importance in theories of molecular structure and in the interpretation of the complexities of chain reactions in gases. Atomic hydrogen,[23] oxygen,[24] and chlorine [25] are readily prepared by electric discharges through the gases at low pressures. The methyl radical, and the less stable ethyl radical, are obtainable by heating the lead tetra-alkyl,[26] by reaction of the alkyl halide with sodium vapour,[27] or with hydrogen atoms,[28] and by heating the vapours of many organic substances.[29] The methylene radical appears to be formed in the decomposition of methane on hot platinum,[30] and the production of the phenyl and the butyl radical has also been described.[31] These radicals may be detected and estimated by their reactions with halogens or with thin films of zinc, antimony, tellurium, etc. The cyanogen radical is produced in the reaction of sodium vapour with cyanogen halides,[32] and the hydroxyl radical, which has a very short life, has also been prepared.[33] The production of new unstable compounds by the interaction of atomic hydrogen or oxygen with other molecules is described by P. Harteck,[34] and the preparation of mono-, di-, and tri-alkyls of arsenic, antimony, and bismuth by the direct interaction of free methyl and ethyl with the elements by Paneth.[35] The most important use of work on free atoms and radicals appears to be in the interpretation of the mechanism of thermal and photochemical reactions. In the photochemical reactions of hydrogen with chlorine or bromine, for example, the reactions

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[21] E. Hückel, *Trans. Faraday Soc.*, 1934, **30**, 40; compare also C. K. Ingold, *ibid.*, p. 52; Pauling and Wheland, *loc. cit.*, ref (20).

[22] *Ibid.*, p. 10.

[23] R. W. Wood, *Phil. Mag.*, 1921, **42**, 729; 1922, **44**, 538; K. F. Bonhoeffer, *Z. physikal. Chem.*, 1924, **113**, 199; E. Boehm and K. F. Bonhoeffer, *ibid.*, 1926, **119**, 385.

[24] E. Wrede, *Z. Physik*, 1929, **54**, 53; P. Harteck and U. Kopsch, *Z. physikal. Chem.*, 1931, [*B*], **12**, 327.

[25] G. M. Schwab and H. Friess, *Naturwiss.*, 1933, **21**, 222; *A.*, 580; *Z. Elektrochem.*, 1933, **39**, 586; *A.*, 1021; W. H. Rodebush and W. C. Klingelhoefer, *J. Amer. Chem. Soc.*, 1933, **55**, 130; *A.*, 232.

[26] F. Paneth and W. Hofeditz, *Ber.*, 1929, **62**, 1335; F. Paneth and W. Lautsch, *ibid.*, 1931, **64**, 2702; R. N. Meinert, *J. Amer. Chem. Soc.*, 1933, **55**, 979; *A.*, 494.

$$\begin{aligned} X + H_2 &\longrightarrow HX + H \quad (X = \mathrm{Cl\ or\ Br}) \\ H + X_2 &\longrightarrow HX + X \\ H + HX &\longrightarrow X + H_2 \end{aligned}$$

have been assumed to explain the experimental results (cf. p. 50). By the use of halogen or hydrogen atoms, each one of these reactions can be separately examined in detail, its efficiency and temperature dependence found, and a direct confirmation of the correctness of the photochemical assumptions obtained. In a similar way, by examining the rates of reactions of hydrogen and oxygen atoms with oxygen and hydrogen molecules, and finding their dependence on the temperature, information can be obtained as to the efficiencies of the reactions :[36]

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[27] H. von Hartel, M. Meer, and M. Polanyi, *Z. physikal. Chem.*, 1932, [*B*], **19**, 139; *Ann. Reports*, 1932, **29**, 43; E. Horn, M. Polanyi, and D. W. G. Style, *Trans. Faraday Soc.*, 1934, **30**, 189; H. von Hartel, *ibid.*, p. 187.

[28] H. M. Chadwell and T. Titani, *J. Amer. Chem. Soc.*, 1933, **55**, 1363; *A.*, 578.

[29] F. O. Rice, W. R. Johnson, and B. L. Evering, *ibid.*, 1932, **54**, 3529; *A.*, 1932, 1108; F. O. Rice, *Trans. Faraday Soc.*, 1934, **30**, 152; J. A. Leermakers, *J. Amer. Chem. Soc.*, 1933, **55**, 3499.

[30] L. Belchetz, *Trans. Faraday Soc.*, 1934, **30**, 170.

[31] M. F. Dull and J. H. Simons, *J. Amer. Chem. Soc.*, 1933, **55**, 3898; F. E. Frey and H. J. Hepp, *ibid.*, p. 3357.

[32] J. Curry and M. Polanyi, *Z. physikal. Chem.*, 1933, [*B*], **20**, 276; *A.*, 573.

[33] K. F. Bonhoeffer and H. Reichardt, *ibid.*, 1928, **139**, 75; *A.*, 1928, 1188; K. F. Bonhoeffer and T. G. Pearson, *ibid.*, 1931, [*B*], **14**, 1; *A.*, 1931, 1215; W. H. Rodebush and M. H. Wahl, *J. Chem. Physics*, 1933, **1**, 696.

[34] *Trans. Faraday Soc.*, 1934, **30**, 134.

[35] F. Paneth, *ibid.*, p. 179.

$$\begin{aligned} H_2 + O &\longrightarrow OH + H \\ H_2 + O + (\text{third body}) &\longrightarrow H_2O \\ H_2O + O &\longrightarrow 2OH \\ O_2 + H + (\text{third body}) &\longrightarrow HO_2 \\ H_2 + O_2 + H &\longrightarrow H_2O + OH \end{aligned}$$

which may play a part in the thermal reaction between hydrogen and oxygen (cf. p. 51). Rice[37] has attempted to explain the mechanism of the decomposition of organic compounds (particularly hydrocarbons, ethers, and ketones) by heat in terms of dissociation into radicals. On the hypotheses (1) that the primary mechanism is a unimolecular splitting of a link in the molecule, (2) that, as the energy of linking of $C{-}H$ is greater than that of $C{-}C$, the latter link splits in preference to the former, and (3) that this primary formation of radicals leads to a chain reaction, he is able to account semi-quantitatively for the actual products found. The view that a $C{-}C$ link splits more easily than a $C{-}H$ link, however, does not accord with many chemical observations. R. Conrad[38] has shown, from experiments on the decomposition of hydrocarbons in a positive-ray discharge tube, that if a hydrocarbon molecule loses one hydrogen atom the tendency is for another $C{-}H$ link to break to form the link $C{=}C$. The mechanism of the photodecomposition of aldehydes and ketones in ultra-violet light, though not yet clear, also shows that a $C{-}H$ link is more easily broken than a $C{-}C$ link; *e.g.*, while the molecule $CH_2{:}O$ decomposes with a quantum efficiency of 1 independently of wave-length,[39] that for the molecule $CMeH{:}O$ falls off with increasing wave-lengths from 1 to 0,[40] and that for the molecule $CMe_2{:}O$ reaches the value of only 0·17.[41] Thermally, too, aldehydes are more easily decomposed than ketones by homogeneous reactions, and at energies of activation much less than the heats of linkage of $C{-}H$ or $C{-}C$. In all reactions of the unimolecular type, it appears that a mechanism involving a bimolecular interaction of two parts of the same molecule, rather than a simple splitting of a link, is more probable; *e.g.*, in the decomposition of acetaldehyde, the hydrogen atom begins to link up with the methvl group before detaching itself from the carbonyl group; and while the C–H and $C–CH_3$ linkages are weakening, the carbonyl group is simultaneously undergoing reorganisation to give carbon monoxide $\mathrm{C}\overset{\leftarrow}{=}\mathrm{O}$. In the slow oxidation of ethane at high pressures, over 60% of the products contain two carbon atoms (chiefly ethyl alcohol and acetic acid), a fact which is difficult to reconcile with the hypothesis of a ready splitting of a C–C link.[42] The absorption spectra shown by aldehydes, as well as by chromyl[43] and sulphuryl chlorides,[44] may well be diffuse owing to overlapping effects of rotational lines rather than because of a unimolecular decomposition of the excited molecule. If so, the difficulties which arise in explaining the photochemical reactions of these substances in terms of "predissociation" disappear; the reactions in fact falling into the bimolecular class.

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[36] K. H. Geib and P. Harteck, *Trans. Faraday Soc.*, 1934, **30**, 131; P. Harteck, *loc. cit.*, ref. (34).

[37] F. O. Rice, *Chem. Reviews*, 1932, **10**, 135; *Trans. Faraday Soc.*, 1934, **30**, 152.

[38] *Trans. Faraday Soc.*, 1934, **30**, 215.

[39] R. G. W. Norrish and F. W. Kirkbride, *J.*, 1932, 1518; *A.*, 1932, 706.

[40] P. A. Leighton and F. E. Blacet, *J. Amer. Chem. Soc.*, 1933, **55**, 1766; *A.*, 682.

[41] G. H. Damon and F. Daniels, *ibid.*, p. 2363; *A.*, 792.

According to modern conceptions of valency, no bond is to be expected to break in a molecule without simultaneous changes in the energies of all the other bonds, so that comparisons between "heats of linkage" and activation energies or photochemical thresholds are to be made on the basis of examination of their differences (representing energies of reorganisation) rather than in expectation of coincidences. The values of the bond energies in a molecule will also be greatly affected by the near approach of a reacting atom. On these views, the old accepted mechanisms of the Walden inversion and of the Beckmann change, which described the effects as an atom approaching and attaching itself to the face of a tetrahedral carbon or other atom, followed by redistribution of the valency links, present no difficulties of electronic interpretation.[45]

The Hydrogen–Chlorine Reaction.

The alleged inhibiting effect of drying on the hydrogen–chlorine photoreaction[46] now appears to be non-existent,[47] and thereby one of the greatest obstacles to the acceptance of the Nernst chain mechanism has been removed. The mechanism of the reaction now appears to be : [48]

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[42] D. M. Newitt and A. M. Bloch, *Proc. Roy. Soc.*, 1933, [*A*], **140**, 426; *A.*, 678.

[43] R. de L. Kronig, A. Schaafsma, and P. K. Peerlkamp, *Z. physikal. Chem.*, 1933, [*B*], **22**, 323; *A.*, 997; Kantzer, *Compt. rend.*, 1933, **196**, 1882; *A.*, 791.

[44] H. W. Thompson, *Nature*, 1933, **132**, 896.

[45] A. R. Olson, *J. Chem. Physics*, 1933, **1**, 418; H. Eyring and M. Polanyi, *Z. physikal. Chem.*, 1931, [*B*], **12**, 279; *A.*, 1931, 688.

[46] Cf. *Ann. Reports*, 1931, **28**, 46.

[47] A. J. Allmand and H. C. Craggs, *Nature*, 1932, **130**, 927; *A.*, 34; G. K. Rollefson and J. C. Potts, *J. Amer. Chem. Soc.*, 1933, **55**, 860; *A.*, 358; F. Bernreuther and M. Bodenstein, *Sitzungsber preuss. Akad. Wiss. Berlin*, Phys.-Math. Klasse, 1933, 6; *A.*, 576.

$$Cl_2 + h\nu \longrightarrow Cl + Cl,$$

followed by the repeating steps

$$\begin{aligned} Cl + H_2 &\longrightarrow HCl + H, \\ H + Cl_2 &\longrightarrow HCl + Cl. \end{aligned}$$

Such chains can also be set up by the artificial introduction of chlorine or hydrogen atoms into a mixture of hydrogen and chlorine.[49] In spite of the simplicity of the chain mechanism, the reaction rate depends in a very complex way on the light intensity and the reactant, resultant, and inhibitor (*e.g.*, oxygen) concentrations; but very complete reaction schemes covering the experimental data can now be formulated.[50] In the absence of oxygen (a difficult impurity to remove), the reaction chains may end by the processes :

$$\begin{aligned} &(1)\ H + HCl \longrightarrow H_2 + Cl\ ^{51} \\ &(2)\ Cl + Cl \longrightarrow Cl_2\ ^{52} \\ &(3)\ Cl + \text{wall} \longrightarrow \tfrac{1}{2}Cl_2 \end{aligned}$$

When reactions (1) and (2) are the controlling ones the reaction rate varies as the square root of the light intensity, just as in the hydrogen–bromine photoreaction, and this has been confirmed by experiment.[53] When reaction (3) is important, the size of the vessel has an influence on the rate.[54] In the presence of oxygen as an inhibitor, new chain-ending processes arise involving the removal of chlorine atoms (as oxides of chlorine) and of hydrogen atoms (ultimately to give water) by oxygen molecules. Experimentally it is found that the removal of the hydrogen atoms is the more important of the two, and it may occur by at least two mechanisms :

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[48] W. Nernst, *Z. Elektrochem.*, 1918, **24**, 335; *A.*, 1919, ii, 208.

[49] W. H. Rodebush and W. C. Klingelhoefer, *J. Amer. Chem. Soc.*, 1933, **55**, 130; *A.*, 232; P. Harteck, *Trans. Faraday Soc.*, 1934, **30**, 134.

[50] R. G. W. Norrish and M. Ritchie, *Proc. Roy. Soc.*, 1933, [*A*], **140**, 99, 112, 713; *A.*, 576, 791; M. Bodenstein and P. W. Schenk, *Z. physikal. Chem.*, 1933, *B*], **20**, 420; D. L. Chapman and J. S. Watkins, *J.*, 1933, 743; *A.*, 915.

[51] Norrish and Ritchie, *loc. cit.*, ref. (50).

[52] The Cl atoms may form Cl_3 molecules without altering the kinetics; (G. K. Rollefson and H. Eyring, *J. Amer. Chem. Soc.*, 1932, **54**, 170; *A.*, 1932, 348; G. E. Kimball and H. Eyring, *ibid.*, p. 3876).

[53] D. L. Chapman and F. B. Gibbs, *Nature*, 1931, **127**, 854; *A.*, 1931, 806; Norrish and Ritchie, *loc. cit.*

[54] D. L. Chapman and P. P. Grigg, *J.*, 1928, 3233; 1929, 2426; *A.*, 1929, 154; 1930, 46.

$$H + H_2 + O_2 \longrightarrow H_2O + OH$$

or

$$H + O_2 \longrightarrow HO_2.$$[55]

These processes are identical with those which are likely to occur in the thermal and the mercury-sensitised photochemical reaction of hydrogen and oxygen.[56]

Miscellaneous Reactions.

It has already been pointed out (p. 48) that experiments on the direct introduction of hydrogen and of oxygen atoms into hydrogen–oxygen mixtures may throw light on the mechanism of the hydrogen–oxygen reaction. Such atoms may also be introduced by photosensitisation : hydrogen atoms by using mercury atoms as sensitiser, or by photodecomposition of ammonia or of hydrogen iodide,[57] and oxygen atoms by the photodecomposition of nitrogen peroxide.[58]

The results, though not yet capable of a full interpretation, show such a similarity to the thermal reaction that it is very probable that atoms are concerned in the chain mechanism of the latter.[59] The behaviour of several other chain reactions has been investigated, *viz.*, the oxidation of phosphine,[60] of triethylphosphine,[61] and of carbonyl sulphide,[62] and the formation of peroxides as chain carriers in the oxidation of acetaldehyde,[63] and of dimethyl- and diethylzinc.[64] The relative values of the inhibiting effects in solution of a large number of inhibitors on the photopolymerisation of vinyl acetate and on the thermal autoxidation of sodium sulphite have been shown to be approximately equal, in agreement with the chain-reaction theory of H. J. L. Bäckström.[65]

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[55] The process $H + HCl + O_2 \longrightarrow H_2O + ClO$ may also occur (R. G. W. Norrish and M. Ritchie, *loc. cit.*).

[56] J. R. Bates, *Proc. Nat. Acad. Sci.*, 1933, **19**, 81; *A.*, 358.

[57] J. R. Bates and D. J. Salley, *J. Amer. Chem. Soc.*, 1933, **55**, 110; J. R. Bates and G. I. Lavin, *ibid.*, p. 81; H. S. Taylor and D. J. Salley, *ibid.*, p. 96. *A.*, 236, 237.

[58] R. G. W. Norrish and J. A. G. Griffiths, *Proc. Roy. Soc.*, 1933, [*A*], **139**, 147; *A.*, 236.

[59] For wall effects in the hydrogen–oxygen reaction, see : C. N. Hinshelwood, E. A. Moelwyn-Hughes, and A. C. Rolfe, *ibid.*, p. 521; *A.*, 469; A. T. Williamson, *J. Amer. Chem. Soc.*, 1933, **55**, 1437; *A.*, 572.

[60] H. W. Melville and H. L. Roxburgh, *Nature*, 1933, **131**, 690; *A.*, 678.

[61] H. W. Thompson and N. S. Kelland, *J.*, 1933, 1231.

[62] C. E. H. Bawn, *J.*, 1933, 145; H. W. Thompson, F. L. Hovde, and A. C. H. Cairns, *ibid.*, p. 208; *A.*, 355.

[63] R. N. Pease, *J. Amer. Chem. Soc.*, 1933, **55**, 2753; *A.*, 913.

[64] H. W. Thompson and N. S. Kelland, *J.*, 1933, 746, 756; *A.*, 917 .

Several new homogeneous unimolecular gas reactions have been investigated : the decompositions of ethyl bromide,[66] of methyl and ethyl azides,[67] and of trichloromethyl chloroformate.[68] As expected, they all tend to become bimolecular at low pressures.[69] The thermal decomposition of ozone and the effect of foreign gases have been further examined.[70]

Careful investigations of the kinetics of the reactions of halogens with reducing agents in aqueous solution show that the reactant may be either the halogen molecule, *e.g.*, chlorine or bromine with phosphorous acid,[71] bromine or iodine with formic acid,[72] or the hypohalous acid formed by hydrolysis, *e.g.*, bromine and the oxalate ion.[73] The trihalide ion does not appear to be a reactant in oxidation reactions, but is the reacting species in the addition of iodine to the β-phenylpropiolate ion.[74] In the photoreactions of bromine and of iodine with the oxalate ion, the free halogen acts as an inner light-filter, the trihalide ion being the photoactive species.[75] From this result it may be concluded that the free halogen atom is ineffective in the reaction, which occurs between X_2' ions formed by photodissociation of the trihalide ion and the oxalate ions HC_2O_4' and C_2O_4''.

The rates and modes of addition of halogen acids to unsaturated organic compounds have been of great interest to the organic chemist on account of the light they throw on electronic configurations and steric effects.[76] An attempt to interpret the observed phenomena in conjugated systems by means of wave-mechanics has been made.[77] It now appears that much of the experimental data on modes of addition must be revised because of the unexpected influence of oxygen. Kharasch and his co-workers [78] have shown that, in absence of oxygen or of added peroxides, hydrogen bromide slowly combines with molecules of the type $CH_2{:}CHX$ ($X = Br, CH_3$, etc.) to give $CH_3{\cdot}CHBrX$. A trace of dissolved oxygen (which forms a peroxide of the unsaturated substance) or of added peroxides causes the addition to take place more rapidly, giving $CH_2Br{\cdot}CH_2X$.[79]

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[65] Cf. *Ann. Reports*, 1928, **25**, 329; K. K. Jeu and H. N. Alyea, *J. Amer. Chem. Soc.*, 1933, **55**, 575; *A.*, 357.

[66] E. L. Vernon and F. Daniels, *ibid.*, p. 922; *A.*, 469.

[67] J. A. Leermakers, *ibid.*, p. 2719, 3098; *A.*, 910, 1017.

[68] H. C. Ramsperger and G. Waddington, *ibid.*, p. 214; *A.*, 232.

[69] Cf. *Proc. Roy. Soc.*, 1927, [*A*], **114**, 84; **115**, 215; **116**, 163.

[70] A. Glissmann and H. J. Schumacher, *Z. physikal. Chem.*, 1933, [*B*], **21**, 323; *A.*, 677; B. Lewis, *J. Physical Chem.*, 1933, **37**, 533.

[71] R. O. Griffith and A. McKeown, *Trans. Faraday Soc.*, 1933, **29**, 611; *A.*, 574.

[72] D. Ll. Hammick, W. K. Hutchison, and F. R. Snell, *J.*, 1925, **127**, 2715; *A* 1926, 32; D. Ll. Hammick and M. Zvegintzov, *J.*, 1926, 1105; *A.*, 1926, 691; A. von Kiss and A. Urmánczy, *Z. anorg. Chem.*, 1933, **213**, 353; *A.*, 1017.

[73] R. O. Griffith, A. McKeown, and A. G. Winn, *Trans. Faraday Soc.*, 1932, **28**, 107; *A.*, 1932, 344; B. Makower and H. A. Liebhafsky, *ibid.*, 1933, **29**, 597; *A.*, 573.

[74] E. A. Moelwyn-Hughes and A. R. Legard, *J.*, 1933, 424; *A.*, 573.

[75] R. O. Griffith, A. McKeown, and A. G. Winn, *Trans. Faraday Soc.*, 1933, **29**, 369; *A.*, 237; E. Abel, H. Schmidt, and K. Retter, *Z. physikal. Chem.*, 1932, **163**, 53; *A.*, 237.

[76] H. Burton and C. K. Ingold, *J.*, 1928, 904; 1929, 2022; *A.*, 1928, 634; 1929, 1270; cf. *Ann. Reports*, 1928, **25**, 121, 128; 1929, **26**, 119.

The decomposition of nitroamine dissolved in *iso*amyl alcohol, as in water, is catalysed by basic ions.[80] From the specific catalytic effect of the HSO_4' ion in the hydrolysis of ethyl acetate, the second dissociation constant of sulphuric acid is calculated to be 10^{-2}.[81]

In aqueous solution the thermal decomposition of ozone is bimolecular, and between p_H 5·3 and 8 it is catalysed by the hydrogen ion. Neutral salts also exert a catalytic effect.[82]

The rates of change and the equilibria in the reactions $CO_2 + H_2O \rightleftharpoons H_2CO_3$ have been measured by methods specially devised to cope with the high velocities in both directions.[83] This equilibrium affects the theory of the rate of dissolution of solid carbonates in acids, as freshly liberated carbonic acid contains more hydrogen ion than the equilibrium mixture.[84]

In addition to the photoreactions already described, mention may be made of the following reactions. In ultra-violet light of wave-length shorter than 2750 Å., chlorine monoxide decomposes with a quantum efficiency of 4·5 at 20°, while at longer wave-lengths the efficiency is about 2. It seems likely therefore that in the two regions two types of decomposition occur : [85] $Cl_2O \longrightarrow 2Cl + O$ and $Cl_2O \longrightarrow Cl + ClO$.

The photodecomposition and oxidation of phosphine [86] and of carbonyl chloride [87] are chain reactions initiated by a process of predissociation. Diazomethane is decomposed by light with a quantum efficiency of about 4, the primary products being probably CH_2 and N_2.[88] Solutions of *N*-chloroacetanilide, when illuminated, give, besides *p*-chloroacetanilide, diacetylhydrazobenzene, chlorinated solvent, and other products, indicating that the primary change may be the liberation of a chlorine atom, as in the case of nitrogen chloride itself.[89]

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[77] H. Eyring, A. Sherman, and G. E. Kimball, *J. Chem. Physics*, 1933, **1**, 586.

[78] M. S. Kharasch and F. R. Mayo, *J. Amer. Chem. Soc.*, 1933, **55**, 2468; M. S. Kharasch and M. C. McNab, *ibid.*, p. 2531; *A.*, 805; J. C. Smith, *Nature*, 1933, **132**, 447.

[79] See also R. P. Linstead and H. N. Rydon, *ibid.*, p. 643.

[80] J. N. Brönsted and J. E. Vance, *Z. physikal. Chem.*, 1933, **163**, 240; *A.*, 471.

[81] H. M. Dawson, E. R. Pycock, and E. Spivey, *J.*, 1933, 291; *A.*, 471.

[82] K. Sennewald, *Z. physikal. Chem.*, 1933, **164**, 305; *A.*, 678.

[83] R. Brinkman, R. Margaria, and F. J. W. Roughton, *Phil. Trans.*, 1933, [*A*], **232**, 65; *A.*, 678.

[84] C. V. King and Cheng Ling Liu, *J. Amer. Chem. Soc.*, 1933, **55**, 1928; *A.*, 679.

[85] H. J. Schumacher and R. V. Townend, *Z. physikal. Chem.*, 1933, [*B*], **20**, 375; *A.*, 577.

[86] H. W. Melville, *Proc. Roy. Soc.*, 1933, [*A*], **139**, 541; *A.*, 473.

The coloured solutions of alkali metals in liquid ammonia are photoactive, and decompose in ultra-violet light to give hydrogen and the metallic amide.[90] The discovery of a method of intensification of weak photographic images, using silver sulphide, has been announced, and may prove of great value in scientific work.[91]

A number of experiments have been made on the effect of supersonic waves, and of sound waves of audible frequency, and of high energy, on chemical reactions. Colloids such as gelatin are depolymerised; but other effects such as the formation of hydrogen peroxide from water and air are claimed. Many of the results obtained are probably due to local heating of the solutions employed.[92]

Preliminary experiments have been described on reaction rates in unimolecular films on water, such as the oxidation of unsaturated acids and ester formation in the layer.[93]

All chemical changes involving solids liberating or reacting with gases show " interface effect," noticed long ago by Faraday in the example of the loss of water from hydrated salts. The reaction takes place wholly at the interfaces between solid reactant and either solid resultant or other suitable solids,[94] and the rate is determined by the rate of growth of the interfaces. These rates of growth may thus be measured from the reaction rate.[95] A serious experimental difficulty, however, is often encountered in measurements on solid–gas reactions, for, if they are reversible, the equilibrium (owing to excessive slowing down of the reaction after it has proceeded some way) often appears to differ considerably if approached from the two sides. Possible reasons for this have been advanced.[96]

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[87] F. Almasy and T. Wagner-Jauregg, *Z. physikal. Chem.*, 1932, [*B*], **19**, 405; G. K. Rollefson and C. W. Montgomery, *J. Amer. Chem. Soc.*, 1933, **55**, 142; G. K. Rollefson, *ibid.*, p. 148; *A.*, 237.

[88] F. W. Kirkbride and R. G. W. Norrish, *J.*, 1933, 119; *A.*, 359.

[89] F. W. Hodges, *J.*, 1933, 240; *A.*, 473.

[90] R. A. Ogg, P. A. Leighton, and F. W. Bergstrom, *J. Amer. Chem. Soc.*, 1933, **55**, 1754; *A.*, 682.

[91] K. Hickman and W. Weigerts, *Nature*, 1933, **132**, 134; *A.*, 915.

[92] A. Szalay, *Z. physikal. Chem.*, 1933, **164**, 234; *A.*, 578; H. Beuthe, *ibid.*, **163**, 161; *A.*, 473; A. Szent-Györgyi, *Nature*, 1933, **131**, 278; *A.*, 359; E. W. Flosdorf and L. A. Chambers, *J. Amer. Chem. Soc.*, 1933, **55**, 3051; *A.*, 915.

[93] A. H. Hughes and E. K. Rideal, *Proc. Roy. Soc.*, 1933, [*A*], **140**, 253; *A.*, 679; S. E. Bresler, W. W. Druschinin, and D. L. Talmud, *Z. physikal. Chem.*, 1933, **164**, 389; *A.*, 672.

[94] G. N. Lewis, *ibid.*, 1905, **52**, 310; I. Langmuir, *J. Amer. Chem. Soc.*, 1916, **38**, 2263; C. N. Hinshelwood and E. J. Bowen, *Phil. Mag.*, 1920, [vi], **40**, 569; *A.*, 1920, ii, 743; *Proc. Roy. Soc.*, 1921, [*A*], **99**, 203; *A.*, 1921, ii, 443.

There appears to be no reason to doubt that interface action is an example of an increase in rate due to the provision of a new path for the reaction with a lower heat of activation.[97] The reactions of metallic oxides with hydrogen, which take place at the interface metal–oxide, have been theoretically examined from this point of view.[98] For the direct attack by hydrogen of cupric oxide, for example, a high heat of activation is necessary because the copper atoms produced must first exist in the adsorbed state on the oxide lattice. At a metal-oxide interface the metal atoms can pass easily to a metallic lattice, and the heat of activation of the reaction is lowered. This view represents only one of many possibilities, however, for in a reaction

$$A_{\text{solid}} + B_{\text{gas}} + X_{\text{solid}} \longrightarrow C_{\text{solid}} + D_{\text{gas}} + X_{\text{solid}}$$

the relative values of the heats of adsorption of the gases B and D on the solids A, C, and X, as well as those of atoms of C on A and X must be considered in any theoretical analysis of problems of reactions of gases with solids (including catalysis and promoter action). The enumeration of the possibilities of different paths for the reaction involving adsorption of the resultants in different ways is easy; the difficulties arise when any attempt is made to discover precisely which particular possibility applies to any one chemical example.

An elaborate investigation into the question of the limits of applicability of the differential aeration theory of metallic corrosion has been carried out.[99] Corrosion is often observed to occur where the simple theory would not predict it, *i.e.*, in places where oxygen is in excess. Dissolved oxygen " passivates " iron, making it cathodic to other iron by forming a film. Under certain conditions, however, the film, particularly when thick and not exposed to free access of oxygen, may apparently crack away, leaving anodic areas where vigorous corrosion may occur, more vigorous even than that on parts of the iron not protected by so thick a film. The phenomenon of " water-line " corrosion is an example of this type of effect. A complete elucidation of all the factors involved is a peculiarly difficult problem. E. J. B.

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[95] W. E. Garner, A. S. Gomm, and H. R. Hales, *J.*, 1933, 1393.

[96] J. Zawadzki and S. Bretsznajder, *Z. physikal. Chem.*, 1933, [*B*], **22**, 60, 79; *A.*, 911.

[97] Cf. C. N. Hinshelwood, " Kinetics of Chemical Change in Gaseous Systems," 3rd edition, Oxford, 1933, pp. 220, 301.

[98] A. R. Ubbelohde, *Trans. Faraday Soc.*, 1933, **24**, 532.

[99] Cf. U. R. Evans, " The Corrosion of Metals," E. Arnold & Co., London, 1926, chap. 6; G. D. Bengough and F. Wormwell, *Proc. Roy. Soc.*, 1933, [*A*], **140**, 399; *A.*, 679.

4. SPECTROSCOPY.

The increasing importance of spectroscopic data in chemistry and the prolific accumulation of new facts and theories since the last report on this subject[1] warrant a somewhat more detailed account of several matters which have hitherto been regarded as purely physical. It is impossible in the length of this report to mention all the relevant topics, or even enter exhaustively into those given; those subjects chosen have not been more than cursorily discussed before. The derivation from spectroscopic material of chemical data, *e.g.*, energies of binding, interatomic distances, angles between valency bonds, theories with regard to the mechanism of chemical change, and the determination of activation energies, has been given elsewhere.[2]

The Energy Levels of Atoms and Molecules.—In contrast to the energy of an atom, which is entirely electronic, the energy of a molecule is of three kinds, electronic, vibrational, and rotational. To a first approximation these can be regarded as additive, although the interaction of rotational motion with that of electrons in their orbits is fundamental in elucidating the fine structure of the bands in the molecular spectrum.[3] It is very largely from a study of the vibration and rotation levels that the chemical data just referred to are obtained. Vibration and rotation of a molecule, however, tend to instability, and the existence of stable molecules is conditioned by electronic energy. An understanding of the electronic configuration of molecules is therefore essential for the correct interpretation of valency. In the sense of the Lewis–Langmuir–Sidgwick theories of electron-sharing this has long been realised. On the other hand, a satisfactory reason for electron-sharing has never been given, and there are strong reasons for believing that its interpretation as a pairing of two electrons antisymmetric in spin is inadequate, and although often fortuitously applicable,[4] not universally valid.[5]

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[1] *Ann Reports*, 1926, **23**, 296; 1929, **26**, 16. See also this vol., p. 79.

[2] *Ibid.*, 1932, **29**, 46; 1931, **28**, 19; N. V. Sidgwick and E. J. Bowen, *ibid.*, 1931, **28**, 367; R. S. Mulliken, *Chem. Reviews*, 1929, **6**, 526; E. Rabinowitsch, *Z. Elektrochem.*, 1931, **37**, 91.

[3] Mulliken, *Rev. Mod. Physics*, 1930, **2**, 87; 1931, **3**, 89.

Ann. Reports, 1930, **27**, 14.

[5] R. S. Mulliken, *Chem. Reviews*, 1931, **9**, 347; 1929, **6**, 503; *Rev. Mod. Physics*, 1932, **4**, 1; *Physical Rev.*, 1932, **41**, 49.

Several summarising papers[6] and monographs have recently appeared on the energy levels and electron configurations of atoms which are a necessary preliminary to the understanding of molecular electronic levels. The energy levels—so-called terms—of hydrogen and ionised helium were found empirically to be of the form R/n^2, and line frequencies were given by the difference of two such terms. Applying the quantum theory Bohr and Sommerfeld satisfactorily explained this result, n being the principal quantum number of the electronic orbit. The terms calculated by the semi-Keplerian method agreed with those observed. Regarding alkalis as built up from a core with one "emitting electron," similar terms should result, but in general the values found are R/n^{*2}, n^* not being integral. This is best interpreted by supposing that n^* is composite and equal to $n + \alpha$, the quantity α arising from a penetration of the core by the orbit of the outer emitting electron. When penetration does not occur n^* becomes integral and the term is said to be hydrogen-like. Some terms differ only slightly from those of hydrogen; in such cases there may be a slight polarisation of the atom core by the emitting electron. With non-hydrogen-like terms, penetration causes the emitting electron to become more firmly bound during part of its orbit, the corresponding increase in the term value implies that n exceeds n^*, and the quantity α, which is then negative, is called the quantum defect. It is clear that the shape of the orbit of the emitting electron will decide the extent of penetration. But the Bohr–Sommerfeld theory introduced a second quantum number k, which, besides measuring the angular momentum of the electron in its orbit, essentially determined the eccentricity of the orbit, and it is consequently to be expected that the value of the quantum defect α will be related to this azimuthal or subsidiary quantum number. It is possible to verify this by determining on the one hand the mean radius of the atomic core, *i.e.*, the radius of the atomic ion, and on the other, the nearest distance of approach of the emitting electron to the nucleus. If the former exceeds the latter, penetration will occur. Mean ionic radii have been calculated for the alkalis wave-mechanically by L. Pauling[7] and by D. R. Hartree,[8] using the electron distribution function $\Sigma 4\pi r^2\psi\bar{\psi}$ for all the electrons † (see below). Further inspection shows that the empirical values of n^* fall into groups, in which the members differ successively by unity, the defects being constant within a group, but differing from one group to another. The quantum defects were expressed as letters s, p, d . . . . , and a term $R/(n + s)^2$ was called an ns term. From the above it is clear that to s, p, d, must be assigned definite values of the subsidiary quantum number k. In the original theory $k = 0, 1, 2 \ldots n$, the zero value being forbidden since it would imply a linear orbit passing through the nucleus; k is now replaced by a new quantum number $l = k - 1$, the change being fully justified in the wave mechanics; and in order to comply with the singlet nature of the s levels and doublet p, d . . . found for alkalis, s electrons are assigned a value $l = 0$, p electrons have $l = 1$, d have $l = 2$, etc. Thus a $4p$ alkali electron means one in a 4 principal quantum orbit with subsidiary quantum number unity, the term being $R/(4 + p)^2$, p being the particular correction value for penetration in this state. Again, it is found that s terms only combine with p terms, p with s and d, d with p and f . . . Expressed differently, this means that there is a selection principle limiting changes of the angular momentum quantum number l to unity, *i.e.*, $\Delta l = \pm 1$. This result would be predicted by considerations of the correspondence principle and is indicated in the wave mechanics. The doublet nature of p, d, f . . . alkali levels, the singlet and triplet alkaline earths, and other systems of multiplet levels imply the presence of a further factor, which was denoted by Sommerfeld as the inner quantum number. G. E. Uhlenbeck and S. Goudsmit [9] first attributed a spin on its own axis to the electron, the spin quantum number s being taken empirically as $\frac{1}{2}$, and the spin angular momentum $\pm \frac{1}{2} \cdot h/2\pi$.‡ Values of the total angular momentum j are then to be obtained by compounding l with s. For alkali s ($l = 0$) electrons, $j = \pm \frac{1}{2}$; for p electrons, $j = 1\frac{1}{2}$ or $\frac{1}{2}$; for d electrons $j = 2\frac{1}{2}$ or $1\frac{1}{2}$, etc. . . . Energetically the two s states are then indistinct, in agreement with fact. The additional selection rule for transitions, $\Delta j = 0$ or ± 1, is also explained theoretically.

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[6] R. C. Gibbs, *Rev. Mod. Physics*, 1932, **4**, 278; S. Dushman, *Chem. Reviews*, 1928, **5**, 109; Hund, "Linienspektren," Springer, 1927; Pauling and Goudsmit, "Structure of Line Spectra," McGraw-Hill, 1930; Jevons, "Band Spectra," Cambridge, 1932, Chap. V; A. Sommerfeld, "Atombau," 5th Edn.

[7] *Proc. Roy. Soc.*, 1927, [*A*], **114**, 181; *A.*, 1927, 394; *J. Amer. Chem. Soc.*, 1927, **49**, 765; *A.*, 1927, 399.

[8] *Proc. Camb. Phil. Soc.*, 1928, **24**, 89, 111; *A.*, 1928, 216.

In order to comply with the nomenclature to be used for other types of atom, the states given by alkali s, p, d . . . electrons are now designated as S, P, D . . . terms. The multiplicity of the level is written above and to the left, and the value of j as a subscript to the right, and the principal quantum number may precede the whole. To retain uniformity, the doublet superscript is retained for the s levels although they are really singlet. Thus $4^2D_{\frac{5}{2}}$ implies that for the emitting electron $n = 4$, $l = 2$, $s = +\frac{1}{2}$, $j = \frac{5}{2}$.

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[9] *Nature*, 1926, **117**, 264; *A.*, 1926, 215.

† $\psi = \psi(x,y,z)e^{2\pi i\nu t}$ is a wave function, *i.e.*, solution of the appropriate Schrödinger equation, and $\psi\bar{\psi}$ is an electric density, independent of time and dependent only on space co-ordinates.

‡ The replacement of angular moments $l \cdot \frac{h}{2\pi}$ by $\sqrt{l(l+1)} \cdot \frac{h}{2\pi}$ and $s \cdot \frac{h}{2\pi}$ by $\sqrt{s(s+1)} \cdot \frac{h}{2\pi}$ is neglected in this report.

Assuming the core-model, alkali terms can be calculated approximately by the methods of Bohr and Sommerfeld. But the difficulties of the many-body problem—helium or higher many-electron atoms—are so far insuperable. Whilst Ca^+ or Al^{++} can be regarded as alkali-like, neutral Ca or Al cannot be treated at all. However, the introduction of electron spin makes the whole system very complicated. The consequent failure of the core model led to the introduction of the vector model in which the various angular momenta of the particles in the system are compounded together quantum vectorially to give the resultant state of the whole. This vector model is invaluable in interpreting the magnetic properties of atoms and in predicting the possible states for a given electronic configuration. As Hund has shown, however, different ways of combining a given set of quantum vectors lead to different results. The most common type of "coupling" found is that named after H. N. Russell and F. A. Saunders,[10] in which the l values of all the electrons are combined, then all the s values, and finally the two resultants L and S. For example, in an atom with two outer electrons not in closed shells * (for which $\Sigma l = 0$, $\Sigma s = 0$), *e.g.*, calcium, if the l quantum numbers are respectively l_1, l_2, and the spins s_1, s_2 ($\pm \frac{1}{2}$), the resultant orbital angular momentum L is one of $(l_1 + l_2)$, $(l_1 + l_2 - 1)$ . . . . . $(l_1 - l_2)$, and the net spin 1 or 0. With the latter spin value each L value will give one total angular momentum $J = L$; with the former there will be three values $L + 1$, L, $L - 1$, and the terms will be singlets and triplets. With three-electron atoms $S = \Sigma s = \frac{1}{2}$ or $\frac{3}{2}$ and $J = L + \frac{1}{2}$, $L - \frac{1}{2}$, or $L + \frac{3}{2}$, $L + \frac{1}{2}$, $L - \frac{1}{2}$, $L - \frac{3}{2}$ giving doublets and

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[10] *Astrophys. J.*, 1925, **61**, 38; *A.*, 1925, ii, 911.

* Electrons of equal n form a shell. A closed shell contains groups of electrons with equal l. In a magnetic field the l level which is $(2l + 1)$-fold degenerate gives $(2l + 1)$ values of the magnetic quantum number m, *i.e.*, $l, l - 1, \ldots\ldots -l$. Since the spin may be $\pm \frac{1}{2}$, there will according to Pauli's principle be $2(2l + 1)$ possibilities for any l group. Since $l = 0, 1, \ldots (n - 1)$, there will be $\sum_{l=0}^{l=n-1} 2(2l + 1) = 2n^2$ electrons in a closed n shell. Closed shells are

$$\underset{K}{[1s^2]} \qquad \underset{L}{[(2s)^2(2p)^6]} \qquad \underset{M}{[(3s)^2(3p)^6(3d)^{10}]}$$

It is obvious how this result applies to the structure of the periodic classification.

quartets. In the same way, four-electron atoms give rise to singlets, triplets and quintets. In this form of coupling the only difference between the singlet and triplet states of given L is difference in spin orientation, which should not be considerable; the rather marked difference in the terms is due to a resonance phenomenon characteristic of the quantum and wave mechanics.[11] Expressions giving the term energies as functions of the quantum numbers are discussed by Hund and by Mulliken.

The atomic terms are called S, P, D . . . according as $L = \Sigma l = 0, 1, 2$ . . . For example, the ground state of carbon $1s^2 2s^2 2p^2$ (*i.e.*, two $1s$ electrons, two $2s$, two $2p$) will have $l_1 = 1$, $l_2 = 1$, and $L = 0$, 1, or 2, giving S, P, or D terms; S will be 0 or 1, giving singlets and triplets. Actually the ground term is ^3P. Similarly, the ground state of nitrogen ($1s^2 2s^2 2p^3$) is ^4S, and that of sodium ($1s^2 2s^2 2p^6 3s$) is ^2S. The total angular momentum quantum number of the entire atom, J, is obtained as before by compounding L and S, *i.e.*, $L + S$, $L + S - 1$, . . . $L - S$, and may be written as a suffix. A further distinction is that atomic states with even values of Σl for all the electrons in the atom are "even" (g) and with Σl odd are "odd" (u). The significance of this can only be satisfactorily understood in terms of the wave mechanics; it can be shown that an even state is such that if its wave function is $\psi(x_1 y_1 z_1 x_2 y_2 z_2 \ . \ . \ .)$, then $\psi(-x_1 - y_1 - z_1 \ . \ . \ .) = \psi(x_1 y_1 z_1 \ . \ . \ .)$, and for an odd state $\psi(-x_1 - y_1 - z_1 \ . \ . \ .) = -\psi(x_1 y_1 z_1 \ . \ . \ .)$. The ground state of carbon is even ($\Sigma l = 2)^3P_g$; of nitrogen odd ($\Sigma l = 3)^4S_n$; of sodium even ($\Sigma l = 6)^2S_g$, and the first excited state $1s^2 2s^2 2p^2 3s$ of nitrogen even ($\Sigma l = 2)^2S_g$. The selection rules for transitions are in general that the total spin shall be unaltered, g terms combine only with u terms, $\Delta L = 0$ or ± 1 and $\Delta J = 0$ or ± 1 with no transition $J = 0 \longrightarrow J = 0$.

Just as the $1s^2 2s^2 2p^2$ state of carbon should give rise to the terms ^1S, ^1P, ^1D, ^3S, ^3P, ^3D, so, in general, a given electronic configuration will provide many terms. F. Hund[12] and J. C. Slater[13] have given rules for determining their relative depths. Usually the greater the multiplicity the lower the term, and for terms of equal multiplicity that one is the lower which has the greater L value. That the ground term of carbon is ^3P rather than ^3D is due to the fact that the configuration leading to ^3D is forbidden by the Pauli principle.*

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[11] W. Heisenberg, *Z. Physik*, 1926, **38**, 411; 1926, **39**, 499; **41**, 239; see also *Ann. Reports*, 1932, **29**, 17; 1931, **28**, 21; 1930, **27**, 14.

[12] *Z. Physik*, 1925, **33**, 345.

[13] *Physical Rev.*, 1926, **28**, 291; 1929, **34**, 1293.

* As a further example helium may be considered. The ground state is $1s^2$. Assuming complete decoupling of the vectors (strong magnetic field),

The splitting of atomic energy levels in a magnetic field is a very important means of deciding their nature, *i.e.*, L value and multiplicity. If the field is " weak," the vectors L and S remain coupled together and precess around their resultant J. The latter precesses around the field axis with a frequency $g \cdot o$, where g is the so-called Landé splitting factor and o the Larmor precession frequency; g depends only on the quantum numbers of the state. The J vector is oriented so as to assume quantised values, $M = J$, $J - 1, \ldots -J$, along the field direction; M is the magnetic quantum number. Each of these orientations has a definite energy value which can be calculated (Zeemann effect).* Thus, a $^1S_0$ level does not split, a $^1D_2$ gives five levels, and a $^2D_{\frac{5}{2}}$ six. There is an additional selection rule $\Delta M = 0$ or ± 1 for transitions.

In a " strong " field, the L,S coupling breaks down, each vector itself precessing with its own frequency about the field direction and giving quantised components M_L and M_S; $M = M_L + M_S$, but the energy relationships are different from those in a " weak " field (Paschen–Back effect). New selection rules, $\Delta M_L = 0$ or ± 1, $\Delta M_S = 0$, replace these for J and M.

In an applied symmetrical electric field the plane of each electronic orbit precesses around the field axis, but the spin vector of the electron is not directly affected by the field. The L vector is controlled by the applied electric field, the S vector only by the magnetic field due to the orbital motion. The details and splitting energies are given in Mulliken's report.[3]

The essential feature of the wave mechanics is Schrödinger's wave equation,[14]

$$\Sigma\frac{1}{m} \cdot \Delta^2\psi + \frac{8\pi^2}{h^2}(E - U)\psi = 0;$$

U is the potential energy of the system, E the total energy, and ψ the wave function, depending on space co-ordinates and time. The imposition of boundary conditions for ψ (it must be finite, continuous, and single-valued at any point, and vanish at infinity) makes it possible to solve the Schrödinger equation only for definite

[14] *Ann. Reports*, 1930, **27**, 13; see also Hinshelwood, *op. cit.*, pp. 36 *et seq.*

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there will be five quantum numbers n, l, s, m_l, m_s. According to Pauli, no two electrons can be identical in n, l, m_l, m_s. In the given case $L = 0$, $S = 0$ or 1, and the possible terms are ^1S and ^3S. In the strong field each electron would have $n = 1$, $l = 0$, $m_l = 0$, $m_s = -\frac{1}{2}$ or $+\frac{1}{2}$. With the first three quantum numbers identical, the spins must be antiparallel, *i.e.*, the state is singlet ^1S. For the configuration $1s2s$, however, the triplet state is also possible since the electrons are now not " equivalent."

* The Stern–Gerlach experiment involves essentially the same process. The splitting of levels actually observed here is determined by M_s.

discrete values of E. If the equation is expressed in spherical polar co-ordinates r, θ, ϕ, and for a hydrogen atom $U = e^2/r$ be substituted, the E values are simply the stationary states of the hydrogen atom. Writing $\psi = R(r)\,\Theta(\theta)\,\Phi(\phi)$, where $R(r)$, $\Theta(\theta)$, $\Phi(\phi)$ are functions of r, θ, and ϕ only, the equation can be " separated " into three complete differential equations each of which only has solutions if certain parameters have proper values. These parameters are the quantum numbers n, $l = 0, 1, 2, \ldots (n - 1)$, and $m = 0, \pm 1, \pm 2 \ldots \pm l$. The ψ's for different states can now be expressed as functions for the co-ordinates and of the quantum numbers. In general ψ passes through several maxima and minima in passing from the nucleus to infinity. Places in which $\psi = 0$ are called nodes, and the frequency of their occurrence is intimately connected with the quantum numbers.[15] Actually, in Cartesians $\psi = \psi\,(x,y,z)e^{2\pi i\nu t}$, where $i = \sqrt{-1}$ so that $\psi\bar{\psi}$ is independent of time. $\psi\bar{\psi}$ represents the electron density at any point specified by the co-ordinates, or the probability that the electron will be found at this point. $\psi\pi r^2 \,.\, \psi\bar{\psi}$ is called the electron distribution function and if this quantity is plotted against r (*i.e.*, nucleus at the origin) the distribution of electricity in the electron cloud is obtained.* For s electrons, $l = 0$ and $\Theta(\theta)\,\Phi(\phi)$ turns out to be constant; in this case ψ depends only on r, *i.e.*, is spherically symmetrical. The electron-distribution function will also be spherically symmetrical in this case. For other, *e.g.*, p, levels, this does not hold, and the particular type of symmetry obtained is important in bond formation.

In cases other than those of hydrogen or ionised helium (the many-body problem again) the wave equation cannot be solved. By using approximations helium has been studied by J. A. Gaunt,[16] E. A. Hylleraas,[17] and I. Waller,[18] lithium by V. Guillemin, jun., and C. Zener,[19] and some other atoms by Zener.[20] Recently a method of solving the equation to obtain atomic terms and wave functions has been achieved by means of the Hartree " self-consistent " field,[21] also used by Slater,[22] V. Fock,[23] and J. E. Lennard-Jones.[24] The self-consistent field for an atom or ion is defined as being such that " the wave functions for the electrons in that field give a distribution of charge which with the nucleus reproduces the field." Hartree replaces the many-body problem by a one-body problem with a central field for each electron. The Schrödinger equation written as a sum for all the electrons in the system is replaced by a sum of separate equations in which the potential is a function of the *i*th electron only. Wave functions of the latter equation can be obtained, and the total atomic wave function expressed as a combination of these one-electron wave functions, so chosen to satisfy Pauli's principle and be antisymmetric in the co-ordinates of all pairs of electrons. J. McDougall [25] has applied the method to Si^{++++} which is a spherically symmetrical core. A certain field is assumed and the simplified Schrödinger equation for each core electron (n,l) is solved. In each case the equation has, for any E value, one solution which is zero at the origin and one which is zero at infinity. For certain values of E these solutions are identical, *i.e.*, they join smoothly at intermediate radii. The approximately correct E value is found by trial and error. By using this, the one-electron wave function ψ_i follows. The sum of the charge densities given by $\psi_i\bar{\psi}_i$ is thus found. This quantity is added for all electrons except one, the potential due to the resulting charge calculated and compared with the field assumed for one electron. Approximations are made again by trial and error until the assumed and the calculated field agree. The sum density distribution then gives the " self-consistent field." The separate characteristic energy values of the one-electron wave equations are very close to the spectral terms. To get the optical terms of Si^{+++}, the entire calculations should now be repeated with introduction of the series electron $3s$, or $4p$. . . . It is, however, possible to regard this series electron as moving in the field of the core Si^{++++}, and solve the Schrödinger equation using the potential given by the self-consistent field. Estimations for thirteen terms agree well with fact; slight discrepancies may be due to a polarisation of the atom core not allowed for. It is interesting to find that for terms of the same value of l the energy values vary widely, but the quantum defects remain the same.

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[15] Darrow, "Einführung in die Wellenmechanik," Hirzel, 1929; Castelfranchi, " Modern Physics," Churchill, 1932, Vol. II, Chap. VIII.

[16] *Proc. Camb. Phil. Soc.*, 1928, **24**, 332; *A.*, 1928, 685.

[17] *Z. Physik*, 1929, **54**, 347; *A.*, 1929, 616; 1930, **65**, 209; 1930, **66**, 453; *A.*, 1931, 143; E. A. Hylleraas and B. Undheim, *ibid.*, 1930, **65**, 759; *A.*, 1931, 4.

[18] *Ibid.*, 1926, **38**, 635; *A.*, 1926, 987.

[19] *Ibid.*, 1930, **61**, 199; *A.*, 1930, 649.

[20] *Physical Rev.*, 1930, **36**, 51; *A.*, 1930, 1234.

* This indicates what is meant by saying that an electron can simultaneously be at more than one point. The " mean " radius of the orbit agrees with that of the old Bohr theory. See Pauling and Goudsmit, *op. cit.*

Hartree's method involves certain approximations in the way the wave functions of the individual electrons are combined to give the entire atomic wave function. Slater and Fock used more accurate forms but their equations cannot be manipulated mathematically. D. R. Hartree and (Miss) M. M. Black [26] have extended the work to calculate the terms, ionisation potentials and multiplet separations of O, O^+, O^{++}, O^{+++}. Lack of spherical symmetry introduces complications, and when a $2p$ electron is removed from O^+ to give O^{++} the wave functions of the remaining $2s$ and $2p$ electrons are noticeably changed; the O^+ is not an unperturbed O^{++} core with added $2p$ electron. D. R. Hartree [27] has now given the atomic wave functions and self-consistent fields for Cl^- and Cu^+. Others soon to be published include Al^{+++}, K^+, Rb^+, Cs^+. It is interesting to compare the results for Cu^+ (Group I*b*) with those for Na^+ (Group I*a*).

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[21] D. R. Hartree, *Proc. Camb. Phil. Soc.*, 1928, **24**, 89; *A.*, 1928, 216.
[22] *Physical Rev.*, 1929, **34**, 1293.
[23] *Z. Physik*, 1930, **61**, 126.
[24] *Proc. Camb. Phil. Soc.*, 1931, **27**, 469; *A.*, 1931, 1109.
[25] *Proc. Roy. Soc.*, 1932, [*A*], **138**, 550; *A.*, 107.

One point not usually made obvious is the exact connexion between the quantum numbers which appear as characteristic parameters of the wave equation and those taken as vector angular momenta in the model used above. The characteristic parameters are connected with a number of nodes. It is, however, possible to formulate the solutions of the wave equation so that the vectorial nature of l is apparent.[28] In the relativistic wave theory the precise nature of s and j should appear too.

If the number of stable electronic levels of a molecule was comparable with the number often found for atoms, the analysis of a band spectrum would be in many cases impossible. Many expected molecule states are, however, unstable, *i.e.*, with purely repulsive potential-energy curves or curves with shallow minima at large r_e; they are nevertheless important in explaining certain continuous spectra * phenomena involving collisions of the second kind, and the pressure broadening of spectral lines. The excitation of a molecule to many states (and their consequent detection) is also to some extent limited by its dissociation under the conditions by vibration into some other state. The observed electron levels of H_2 and He_2 closely resemble the He term diagram; there are singlets and triplets, the relative depths and multiplet separations being similar. A. Fowler [29] first noticed that some of the levels could be expressed as Rydberg terms R/n^{*2} and band heads given by difference of terms as for atoms. Moreover, as Mulliken first realised,[30] the few lowest known electron levels of CN, N_2^+, CO^+, BO, BeF, MgH, each containing thirteen electrons, are closely similar to those of Na and Mg^+. This might be expected if the atoms each retained their two $n = 1$ (K electrons) and shared an octet of eight $n = 2$ electrons, leaving one $n = 3$ outer or valency electron. In these circumstances the 21-electron molecules SiN, AlO, MgF should have similar levels to K or Ca^+. Some analogy is found, but there is ample evidence to indicate that the close parallel between Rydberg atom levels and molecule terms cannot be sustained.* Mulliken[31] has explained the matter fully, indicating why Rydberg-like terms arise for H_2 and He_2.

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[26] *Proc. Roy. Soc.*, 1932, [*A*], **139**, 311; *A.*, 202.

[27] *Ibid.*, 1933, [*A*], **141**, 282; see also J. C. Slater, *Physical Rev.*, 1929, **35**, 210; 1932, **42**, 33; *A.*, 1932, 1187.

[28] E. Rabinowitsch, *Z. Elektrochem.*, 1931, **38**, 370; W. Weizel, "Bandenspektren," Handb. expt. Physik (Ergänzungsband).

[29] *Proc. Roy. Soc.*, 1915, **91**, [*A*], 208.

* The hydrogen continuum produced in a low-pressure discharge tube is due to a transition from the stable excited $(1s\sigma)(2s\sigma)^3\Sigma_g{}^+$ state to the unstable $(1s\sigma)(2p\sigma)^3\Sigma_u^+$ (W. Finkelnburg and W. Weizel, *Z. Physik*, 1931, **68**, 577).

The vector model is fundamental for an understanding of the electronic levels of molecules.[32] An outer electron may be regarded as moving in the electric field due to the core. In diatomic molecules this field is axially (not spherically) symmetrical along the internuclear axis. The term values should then be analogous to those obtained from the " united atom " in a strong electric field (Stark effect). There should be groups of levels, as in the atom groups, of different M_L, each with sub-levels of different M_S. Briefly, the L vector is resolved along the internuclear axis to give a new quantum number Λ. In place of M_L, M_S, and M, the symbols Λ, Σ and Ω are used. $\Lambda h/2\pi$ and $\Sigma h/2\pi$ are the components of the orbital and spin angular momenta along the internuclear axis, and $\Omega \, . \, h/2\pi$ is the component of the total angular momentum along this axis. The unresolved orbital and spin angular momenta are determined by L and S. $\Lambda = M_L$ can take the values 0, 1, 2 . . . L, but in the absence of perturbations every level with $\Lambda > 0$ will be doubly degenerate, owing to the two opposite directions of revolution ($\pm M_L$). The presence of molecular rotation will remove this degeneracy (Λ-type doubling; compare Jevons, *op. cit.*, p. 126). $\Sigma = S, S - 1, \ldots . -S$, and $\Omega = \Lambda + \Sigma = (\Lambda + S) \; (\Lambda + S - 1) \ldots . (\Lambda - S)$. Λ, Σ, Ω really replace L, S, and J in the notation for atomic levels; terms with $\Lambda = 0, 1, 2 \ldots$ are Σ, Π, Δ . . . states like the S, P, D . . . levels of atoms. ${}^2\Pi_{\frac{1}{2}}$ means $\Lambda = 1$, $S = \frac{1}{2}$, $\Sigma = -\frac{1}{2}$, $\Omega = \frac{1}{2}$. Two other classifications are necessary: + and − terms are distinguished according to the symmetry or asymmetry of the wave function with respect to a reflexion in any plane passing through the nuclei;

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[30] R. S. Mulliken, *Physical Rev.*, 1925, **26**, 561.

[31] *Idem*, *Rev. Mod. Physics*, 1932, **4**, 59.

[32] Hund, " Linienspektren "; Mulliken, *Rev. Mod. Physics*, 1930, **2**, 60.

* *E.g.*, G. Herzberg, *Z. Physik*, 1929, **52**, 815; R. C. Johnson and R. K. Asundi, *Proc. Roy. Soc.*, 1929, **123**, [*A*], 560.

even (g) and odd (u) levels are distinguished when the nuclei of a diatomic molecule are similar according to the symmetry or asymmetry of the wave function with respect to a reflexion through the mid-point of the line joining the nuclei. As in atoms, states with Σl even are g; those with Σl odd are u. The selection rules for transitions are similar to these in the Stark effect, $\Delta S = 0$ or rarely ± 1, *i.e.*, change in multiplicity zero or rarely 2, also $\Delta \Lambda = 0$ or ± 1, $\Delta \Sigma = 0$. In addition $g \rightleftharpoons u$ and $+ \rightleftharpoons +$ or $- \rightleftharpoons -$.

The analogy with atomic nomenclature is further preserved in describing the individual electronic-quantum numbers.[33] To any electron are assigned four quantum numbers n, l, λ, and s, where n, l, and s have the usual meaning, and λ is the measure of the component of orbital angular momentum along the internuclear axis. Electrons with $l = 0, 1, 2, \ldots$ are s, p, d electrons, and those with $\lambda = 0, 1, 2 \ldots$ are σ, π, $\delta \ldots$ electrons.* A $4p\sigma$ electron means one with $n = 4$, $l = 1$, $\lambda = 0$. Very often, however, the n,l quantum numbers of molecular electrons cannot be specified and have no real meaning. This corresponds with the inability to " separate " the appropriate Schrödinger equation into elliptical co-ordinates.[34] The λ quantum number in such cases nevertheless remains distinct. Mulliken refers to such electrons as $x\sigma$, $y\sigma$, $w\pi$, . . . etc. Lennard-Jones[35] has used $\sigma 1s$, $\sigma^* 1s$, $\pi 2p$, . . . etc., where the symbols $1s$, $2p$ . . . following the σ or π imply definite genetic connexions with electrons of the separate atoms. Often the symbols KK are used to represent the four most firmly bound electrons in a molecule, these being essentially unchanged inner K electrons of the combining atoms. As in atoms, closed shells exist in molecules. According to Pauli, no two electrons can occupy identical n, l, λ orbits (be equivalent) unless their spins are antiparallel. It follows that two equivalent σ electrons will form a closed shell σ^2, four π electrons (two $+\lambda$, two $-\lambda$) π^4, four δ (two $+\lambda$, two $-\lambda$) δ^4. It is also clear that in any closed shell $\Lambda = 0$ and $S = 0$, *i.e.*, a $^1\Sigma$ state.

The molecule terms arising from a given electron configuration are now obtained in the same way as those for atoms. One σ electron gives a $^2\Sigma^+$ term; one π electron gives $^2\Pi$; three equivalent π electrons (π^3) give $^2\Pi$. Two equivalent π electrons (π^2) give $^1\Delta$ ($m_{l_1} = m_{l_2} = \pm 1$, $M_L = \pm 2$, *i.e.*, $\Lambda = 2$ but $S = 0$ by Pauli's principle because $m_{l_1} = m_{l_2}$), $^1\Sigma^+$ and $^3\Sigma^-$ ($m_{l_1} = +1$, $m_{l_2} = -1$,

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[33] R. S. Mulliken, *Chem. Reviews*, 1929, **6**, 503.

[34] W. Weizel, *op. cit.*, ref. (28).

[35] J. E. Lennard-Jones, *Trans. Faraday Soc.*, 1929, **25**, 668; *A.*, 1929, 1360.

* With equal nuclei even and odd electrons must be distinguished, *e.g.*, σ_g and σ_u according to symmetry properties.

$\Lambda = 0$, and $S = 1$, as well as $S = 0$ since $m_{l_1} \neq m_{l_2}$). Other examples are given by Mulliken,[36] F. Hund,[37] and G. Herzberg.[38] Hund has discussed the dependence of the energy on Λ and S for a given electron configuration; as in atoms, for a given value of Λ terms of highest multiplicity lie lowest.

It is impossible here to enter into the application of the wave equation to the study of diatomic molecules. Pauling [39] has given an account of the calculations for H_2 and H_2^+. An excellent and detailed treatment can be found in Weizel's book. The results give full substantiation to the vector model described above. It may also be observed that the method of the Hartree self-consistent field may prove very valuable in this connexion.

The splitting of a level under the influence of a magnetic field, often used to determine the nature of atomic levels, is not very suitable for deciding experimentally the type to which a molecular state belongs, for the splitting is as a rule very complicated and the spectrum analysed with difficulty. The simplest and most usual criterion employed is to study the rotation fine structure in a band involving transitions to or from the level. Other properties of a state, *e.g.*, magnetic character, are sometimes used.

The theoretical prediction and discussion of the electronic levels of diatomic molecules in terms of the vector model has been contributed mainly by F. Hund,[40] R. S. Mulliken,[41] and W. Heitler and G. Herzberg.[42] Three lines of approach have been followed. First, the "united atom" isoelectronic with the molecule to be considered may be hypothetically subjected to an axially symmetric electric field, the nucleus being split in the desired manner. The terms and configurations of the resulting molecule should follow from the original atomic terms and configurations. For example, the lowest levels of the nitrogen atom ($1s^2 2s^2 2p^3$) are ^4S, ^2D, ^2P. It can be shown * (Hund, Mulliken, *locc. cit.*) that in the field (Stark effect) these terms respectively give rise to the molecular states for CH $^4\Sigma^-$; $^2\Sigma^-$, $^2\Pi$, $^2\Delta$; $^2\Sigma^+$, $^2\Pi$. The known states of the CH molecule are $^2\Sigma^-$, $^2\Pi$, $^2\Delta$, $^2\Sigma^+$, and the absence of $^4\Sigma^-$ is probably to be explained by the weak transitions from this quartet to the other doublets. The second $^2\Pi$ state is probably unstable. If, instead of considering what happens to the terms themselves, *i.e.*, to Λ and S, the changes in the electron configuration are followed under the field's action, three possibilities arise, the $(1s)^2(2s)^2(2p)^3$ becoming

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[36] *Rev. Mod. Physics*, 1932, **4**, 10.

[37] *Z. Physik*, 1930, **63**, 727; *A.*, 1930, 1226.

[38] "Molekülstruktur," Hirzel, 1929, p. 175.

[39] *Chem. Reviews*, 1928, **5**, 173.

[40] *Z. Physik*, 1926, **36**, 657; *A.*, 1926, 657; **37**, 742; 1927, **40**, 742; *A.*, 1927, 183; **42**, 93; *A.*, 1927, 495; 1930, **63**, 719; *A.*, 1930, 1226; *Z. Elektrochem.*, 1928, **34**, 441; *Ergeb. exakt. Naturwiss.*, 1929, **8**.

[41] *Physical Rev.*, 1928, **32**, 186, 761; *A.*, 1928, 1067; 1929, 116; 1929, **33**, 730; *A.*, 1929, 740; *Rev. Mod. Physics*, 1932, **4**, 1.

[42] *Z. Physik*, 1929, **53**, 52; *A.*, 1929, 629; G. Herzberg, *ibid.*, **57**, 601; *A.*, 1929, 1367; also "Molekülstruktur," p. 167.

* S terms ($L = 0$) only give $\Sigma(\Lambda = 0)$; D terms ($L = 2$) give $\Sigma(\Lambda = 0)$, $\Pi(\Lambda = 1)$, $\Delta(\Lambda = 2)$, and P terms ($L = 1$) give $\Sigma(\Lambda = 0)$ and $\Pi(\Lambda = 1)$.

$$(1s\sigma)^2(2s\sigma)^2(2p\sigma)^2(2p\pi)$$
or
$$(1s\sigma)^2(2s\sigma)^2(2p\sigma)(2p\pi)^2$$
or
$$(1s\sigma)^2(2s\sigma)^2(2p\pi)^3$$

(An s electron can only become σ, a p either σ or π.) The first state gives a $^2\Pi$ term; the second $^4\Sigma^-$, $^2\Sigma^-$, $^2\Delta$, $^2\Sigma^+$; and the third $^2\Pi$, *i.e.*, the same result is obtained as before. For further details Hund and Mulliken's papers should be consulted. The method is fairly successful for hydrides of the type given, but not so good for other molecules.

The second procedure is to bring together the neutral atoms and find the molecule terms arising from given atomic terms. Hund (*loc. cit.*) and E. Wigner and E. E. Witmer[43] have given the rules involved. The resultant spin vector $S = (S_1 + S_2) \; . \; . \; . \; . \; (S_1 - S_2)$; the orbital angular momentum vectors L_1 and L_2 quantise themselves along the internuclear axis and then combine to give Λ;[44] *e.g.*, O(^3P) + excited N(^2D) give one each of $^2\Phi$, $^4\Phi$, two each of $^2\Delta$, $^4\Delta$, three each of $^2\Pi$, $^4\Pi$, three each of $^2\Sigma$, $^4\Sigma$. Again, normal nitrogen (^4S) + O(^3P) give one each of $^2\Pi$, $^4\Pi$, $^6\Pi$ and one each of $^2\Sigma$, $^4\Sigma$, $^6\Sigma$.

If the approaching atoms have equal nuclei and are not in the same state, twice as many levels result from the exchange degeneracy, each of the above occurring as an even and an odd term. With equal nuclei in the same state the degeneracy disappears but the terms are alternately even and odd.

It is interesting to observe that two normal oxygen atoms (^3P) give rise to $^3\Sigma_u^-$, $^3\Sigma_u^-$, $^3\Sigma_g^+$ terms which do not combine with each other; consequently, the upper level involved in the atmospheric oxygen bands must be formed from one normal and one excited atom, an important fact in estimating the energy of dissociation of oxygen.[45] It is not possible, however, to give general rules for determining the quantum numbers of the individual molecular electrons resulting from the union of two atoms in specified L, S, J states.

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[43] *Z. Physik*, 1928, **51**, 859; *A.*, 1929, 117.

[44] See Kronig, "Band Spectra and Molecular Structure," Cambridge, 1930, pp. 24—25.

[45] G. Herzberg, *Z. physikal. Chem.*, 1929, [*B*], **4**, 223; *A.*, 1930, 277; 1930, [*B*], **10**, 189; *A.*, 1930, 1524.

The third line of approach is essentially that of molecule building used by Bohr for atoms. The wave functions and energy levels of one electron in the presence of the nuclear skeleton are first determined, and the electrons are then added one at a time, going into the lowest available orbits, mutual electronic interactions being ignored. If the electron configuration can be determined in this way the terms are deduced as above. The relationships are, however, more complicated than in atoms, since the orbit types are more varied, and the order of binding depends, not only on the atomic numbers of the nuclei, but also on internuclear separations and other factors.[46] The advantage of the method, especially over the previous ones, is that it explains the similarity in term schemes and physical properties of different isoelectronic molecules. Moreover, in deducing the terms of nitrogen and carbon monoxide from N + N and C + O by the second method, there is no indication of which are the molecular ground states and why they are identical in the two cases. J. E. Lennard-Jones[47] first applied this method of electron configuration and called it the method of molecular orbitals. Molecular orbits (one-electron wave functions) were calculated for such molecules as nitrogen, oxygen, and fluorine; it was concluded that some electrons should be shared whilst others remain localised round a particular nucleus (cf. $\sigma 1s$, $\sigma^* 1s$, $\pi 2p$ above). The extent of sharing was one of degree only. Localised electrons were in atomic orbitals or levels. E. Hückel[48] used a similar method to study the properties of a C=C double bond. He formulated the latter as consisting of two electron pairs $[\sigma]^2[\pi]^2$, where σ has a rotational symmetry about the C—C axis and π has an angular distribution proportional to sin ϕ ($\phi = 0$ in the common plane of all nuclei). The stability of the double bond to rotation is connected with the properties of the $[\pi]_{\sin\,\phi}$ orbital. For nuclei which are not very different, Hund, Herzberg, Mulliken, and Weizel[49] have estimated the order of electron levels and the approximate way in which it changes with changing internuclear separation. In this connexion ionisation potentials are useful. They have given rules (assignment or correlation rules) for stating the atomic level which will give rise to any particular molecular level when the atoms are brought together.

Although predicting the possible molecular terms, none of the procedures above outlined originally indicated whether the levels corresponded to stable states or not. Heitler and London first gave a quantum-mechanical explanation of binding with special reference to hydrogen, the interacting atoms being in S states.[50] They also calculated the energy of interaction. Band-spectrum data in the normal ${}^1\Sigma$ states of H_2, Li_2, Na_2, each formed from two normal ${}^2S$ atoms, are in good agreement with theory; the predicted ${}^2\Sigma$ repulsion state of H_2 is also known. But there are very many disagreements, *e.g.*, according to theory two normal ${}^1S$ atoms should only give rise to a repulsive ${}^1\Sigma$ state, whereas cases are known (Ca_2, Zn_2, Hg_2) of stable molecules. Again the theory fails to explain the stability of oxygen and the ${}^3\Sigma$ ground state of this molecule. Extension of the theory by Heitler[51] and others so as to include interaction of P terms has not proved very successful, and the attempts to generalise it into a theory of spin valency in which valency bonds involve a pairing of two electrons antisymmetric in spin must be regarded as unacceptable.[52] Nevertheless it is important to remember the Heitler and London method of calculating energies of molecule formation.

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[46] R. S. Mulliken, *Rev. Mod. Physics*, 1932, **4**, 40, 41.

[47] *Trans. Faraday Soc.*, 1929, **25**, 668; *A.*, 1929, 1360.

[48] *Z. Physik*, 1930, **60**, 423; *A.*, 1930, 525; *Ann. Reports*, 1930, **27**, 17; 1931, **28**, 17.

[49] *Z. Physik*, 1930, **59**, 320; *A.*, 1930, 394.

Herzberg has attempted to explain the stability or instability of a molecule by enquiring whether in its formation the atomic electrons are moved to a higher or a lower level. The potential-energy curve of a molecule can then be regarded approximately as the superposition of all the separate potential-energy curves of the individual electrons, measured as the atoms approach. Electrons will then be of two types, bonding and antibonding, according to whether they contribute a positive or a negative amount of energy to the binding. A stable molecule will be formed when the number of bonding electrons exceeds the number of antibonding ones. Herzberg suggests that the number of bonding pairs minus that of antibonding pairs gives the valency of a bond, and explains satisfactorily the facts for simple molecules such as H_2^+, H_2, He_2, Li_2, N_2, O_2.

Mulliken has arrived at the idea of bonding and antibonding electrons too. In the formation of ${}^2\Pi$ CH from ${}^3P$ carbon and ${}^2S$ hydrogen,

$(1s)^2(2s)^2(2p)^2, {}^3P + 1s, {}^2S \longrightarrow (1s\sigma)^2(2s\sigma)^2(2p\sigma)^2(2p\pi), {}^2\Pi$ or in other similar processes, it is seen that $1s$ hydrogen electron has become "promoted," *i.e.*, its principal quantum number has increased. This promotion, which can be regarded as a continuous process as the atoms approach, occurs with a number of electrons in the formation of CN, CO, N_2, etc. Mulliken points out from examples that, in general, promoted electrons tend to give repulsive potential-energy curves. He regards a promoted electron as antibonding, and attributes in general to any electron a bonding power which may be positive, negative, or zero. Mulliken's terminology differs from that of Herzberg in the sense that a promoted electron could, according to the latter, in certain circumstances, be bonding; but their essential ideas are similar. In a later paper Mulliken discusses this point and introduces the term premotion.

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[50] *Ann. Reports*, 1930, **27**, 14; R. H. Fowler, *Rep. Brit. Assoc.*, 1931, p. 226.

[51] W. Heitler, *Physikal. Z.*, 1930, **31**, 185; *A.*, 1930, 525; J. H. Bartlett, *Physical Rev.*, 1931, **37**, 507; *A.*, 1931, 548.

[52] R. S. Mulliken, *Chem. Reviews*, 1932, **9**, 347; Herzberg, "Molekülstruktur."

Mulliken has attempted to generalise the idea of bonding power of electrons with a theory of valency.[52] For example, in the formation of H_2 two processes are possible:

$$\mathrm{H}(1s) + \mathrm{H}(1s) \longrightarrow \mathrm{H}_2((1s\sigma)^2\ {}^1\Sigma_g{}^+)$$

or

$$\mathrm{H}(1s) + \mathrm{H}(1s) \longrightarrow \mathrm{H}_2(1s\sigma,\ 2p\sigma\ {}^3\Sigma_u{}^+).$$

In the former case the two electrons are bonding and a stable molecular state results; in the second case the promotion energy of the $1s$ electron to the $2p\sigma$ state is so large that it more than balances that gained by the firmer binding of the $1s\sigma$ electron, hence no stable molecule is formed.

In the union of two helium atoms there would similarly be four $1s$ electrons; in accordance with the Pauli principle, two of these must be promoted and the antibonding effect prevents molecule formation. With one excited helium atom this difficulty would, however, not necessarily arise.

Mulliken stresses the fortuitous nature of antisymmetric spin arrangements in the Heitler–London theory and points out that some molecules (*e.g.*, NaH) have states in which the pair of electrons forming the bond have parallel spins, whilst other cases exist in which one electron appears to bring about a bond. He discusses in detail the structure of many molecules and explains the saturation of valencies in terms of closed shells. He prefers to regard valency, not as a whole-number property of atoms, but as a more flexible quantity depending upon variable electronic bonding powers, the occurrence of bonding electrons in pairs being incidental as far as chemical binding is concerned.

In a critical review of the various methods used in the theory of valency, Hund [53] also apparently concludes that the properties of molecules are more likely to be interpreted in terms of molecular orbitals than in terms of electron-pair bonds. G. N. Lewis has recently reviewed the theory of the electron-pair bond.[54]

[53] *Z. Physik*, 1931, **73**, 1; *ibid.*, 1932, **73**, 565; *A.*, 1932, **10**, 215.

[54] *J. Chem. Physics*, 1933, **1**, 17; *A.*, 211.

Mulliken's report [55] contains a valuable and exhaustive computation of the potential-energy curves of most of the electron states of many diatomic molecules.

The first important wave-mechanical calculations on the structure of polyatomic molecules were made by Pauling [56] and J. C. Slater,[57] using what has been called the method of electron-pair bonds. Their work consists essentially in a generalisation of the Heitler–London theory, but instead of considering the interaction of atoms in definite states they suggest that in the presence of the strong perturbation such as occurs in molecule formation the atomic states should not be treated separately but merged together. They determine new atomic wave functions which are hybrids of the usual ones and are able to associate definite directions with each. This leads to the idea of directed (orbital) valency. The interaction of two wave functions, belonging severally to an electron in each atom, is considered, and the maximum degree of bonding is assumed to result when the wave functions overlap to the greatest extent. The theory has been very successful in interpretation of the covalent link. One objection often raised to it is that it involves a hybridisation of the *s*, *p* wave functions.

Mulliken and others have developed the alternative method of molecular orbitals or one-electron wave functions for polyatomic molecules. Both atomic and molecular orbitals may be thought of as defined in accordance with the Hartree method of the self-consistent field. Unshared electrons are described in terms of atomic orbitals, and shared electrons in terms of molecular orbitals. The underlying idea comes from the work of H. Bethe,[58] who examined the perturbation of the orbitals of an atom when surrounded by other atoms in a crystal. By methods of group theory, he showed how the *s*, *p*, *d* . . . levels of an atom split under perturbations of different symmetry. E. Wigner [59] extended the work to include all the 32 classes of crystal symmetry. G. Placzek [60] has further elaborated the result with special reference to nuclear vibrations in polyatomic molecules. The novelty lies in the consideration of the effect of symmetry properties on orbitals in molecules belonging to one of the 32 symmetry point groups, the symmetry being given by the nuclear skeleton. This leads to the electronic configurations of the molecules.

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[55] *Rev. Mod. Physics*, 1932, **4**, 1.

[56] *J. Amer. Chem. Soc.*, 1931, **53**, 1367, 3225; *A.*, 1931, 670, 1356; 1932, **54**, 988, 3570; *A.*, 1932, 561, 1191; *Ann. Reports*, 1931, **28**, 287, 367; Fowler, *Rep. Brit. Assoc.*, *loc. cit.*, ref. (50).

[57] *Physical Rev.*, 1931, **37**, 481; *A.*, 1931, 548; 1931, **38**, 325, 1109; *A.*, 1931, 1113, 1356.

[58] *Ann. Physik*, 1929, [v], **3**, 133; *A.*, 1929, 1367.

[59] *Nach. Ges. Wiss. Göttingen*, Math. Klasse, 1931.

[60] Marx's "Handb. der Radiologie," 1933.

In his first paper, Mulliken [61] considers four types of symmetry : regular tetrahedral (CH_4), in which p levels do not split; linear (OH', HF), in which p splits into σ and π; trigonal pyramidal (NH_3, $OH_3^{\cdot}$), in which p splits into $[\sigma]$ and $[\pi]$, a somewhat modified σ and π; and finally isosceles triangular (H_2O), in which p splits into three types designated a, b, c. The amounts of splitting can be estimated by group theory. The σ orbitals are non-degenerate, π two-fold degenerate. The appropriate molecular structures are then as follows :

$$OH^-, HF : 1s^22s^22p\sigma^22p\pi^4; \; NH_2^-, H_2O : 1s^22s^22pa^22pb^22pc^2;$$
$$H_3O^+, NH_3 : 1s^22s^22p[\pi]^42p[\sigma]^2; \; NH_4^+, CH_4 : 1s^22s^22p^6.$$

A comparison of the structures of carbon tetrafluoride and tetraiodide is interesting. In the former case the electrons around the carbon atom probably constitute from the latter's point of view closed shells, $1s^22s^22p^6$; the other electrons in the molecule, *i.e.*, those especially attached to the fluorine, are probably very remote from the carbon. From the point of view of the fluorine nucleus there are $1s^22s^22p^6$, but the rest of the molecule sets up a field of the trigonal type and splits up the $2p^6$ into $2p[\sigma]^2$, $2p[\pi]^4$, of which $2p[\sigma]^2$ are shared with the carbon nucleus. The four pairs $2p[\sigma]^2$ of the fluorine atoms are then all shared with the carbon, which regards them as constituting its outer shell $2s^22p^6$. Comparison of this result with that for the tetraiodide leads, when estimates of the wave functions are made, to the idea that about six electrons only (not eight) hold the four halogen atoms in the iodide. Thus this tetraiodide is unstable.

The structures of BF_4^-, SO_4^{--}, ClO_4^-, SO_3^{--}, and ClO_3^- are also discussed on the basis of assumed symmetry. With the last, unshared electrons are found, in agreement with the work of W. H. Zachariasen.[62] The linear molecule of carbon dioxide is shown to be $\sigma^2\sigma^2\sigma^2\sigma^2\sigma^2\sigma^2\sigma^2\pi^4\pi^4$, which agrees with its diamagnetic character. In the case of $PtCl_4^{--}$ the splitting of orbitals is considered.

In a more detailed paper, Mulliken [63] reviews critically the Lewis theory of valency, comparing the properties of molecular orbitals with those of electron-pair bonds. He points out that many rules known about valency find interpretation in the occurrence and behaviour of non-degenerate and degenerate orbitals: *e.g.*, O_2 is . . . . π^2, the π molecular orbital is two-fold degenerate, so that the electrons may have parallel spin, $S = 1$, giving the known $^3\Sigma^-$ state. It is not necessary to have two electrons to get a bond : one electron in a bonding orbital has a bonding effect.*

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[61] *Physical Rev.*, 1932, **40**, 55; *A.*, 1932, 562.

[62] *J. Amer. Chem. Soc.*, 1931, **53**, 2123; *A.*, 1931, 897.

[63] *Physical Rev.*, 1932, **41**, 49; *A.*, 1932, 902.

The molecular orbitals are expressed in zeroth approximations as linear combinations of atomic orbitals. If in the union of H(1*s*) and H^+, the 1*s* atomic orbitals for the respective nuclei are ϕ_A and ϕ_B, the molecular orbitals will be

$$\phi_0 = c_0(\phi_A + \phi_B)\,;\ \phi_1 = c_1(\phi_A - \phi_B),$$

where c_0, c_1 are normalising factors depending on the nuclear separation. The energy change in the binding can be understood by considering the mean charge density $e^2\phi^2$ corresponding to each molecular orbital:

$$\phi_0^2 = c_0^2(\phi_A^2 + \phi_B^2 + 2\phi_A\phi_B)\,;\ \phi_1^2 = c_1^2(\phi_A^2 + \phi_B^2 - 2\phi_A\phi_B).$$

This shows that $e^2\phi_0^2$ is relatively more concentrated in the region between the nuclei than if a mere overlapping of $e^2(\phi_A^2 + \phi_B^2)$ occurred ; on the other hand, ϕ_1^2 is relatively much less concentrated. This added or diminished concentration is decisive in making ϕ_0 bonding and ϕ_1 antibonding. The procedure can be applied to more complicated symmetrical and to unsymmetrical molecules, the appropriate linear combinations of each atomic orbital being taken. It is clear that in order to have a large bonding energy $\phi_A\phi_B$ should be large, which implies a large overlapping of atomic orbitals. This is Pauling and Slater's criterion of bond formation ; the point here is that overlapping orbitals are demanded only, regardless of whether the resulting molecular orbital is occupied by two electrons, by one, or by none. A molecular orbital which is occupied by two electrons might be regarded as being essentially the same as an electron-pair bond.

F. Hund [64] has arrived at similar conclusions to the above. M. Dunkel's work [65] is also important. In two further papers Mulliken [66] has explained in detail the method of applying Bethe's results to determine the number, spacing, and degeneracy of electron states of a molecule, and the transition possibilities. It is necessary in the language of group theory to know the different " irreducible representations " of the symmetry group for the given nuclear skeleton. Applying the theory to CH_2 and hence to ethylene, two cases are considered ; in one the CH_2 radicals are " planar " to each other, in the other they are perpendicular. The normal state of " planar " ethylene turns out to be

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[64] *Z. Physik*, 1931, **73**, 1, 565; *A.*, 1932, 10, 215; 1932, **74**, 429; *A.*, 1932, 449.

[65] *Z. physikal. Chem.*, 1930, [*B*], **7**, 81; [*B*], **10**, 434; *A.*, 1930, 525.

[66] *Physical Rev.*, 1932, **41**, 751; *A.*, 1932, 1190; 1933, **43**, 279; *A.*, 339.

* Pauling has also suggested the possibility of one-electron links.

$$1s^2 1s^2 [s]^2 [s]^2 [y]^2 [y]^2 [z + z]^2 [x + x]^2 \text{ singlet,}$$

and the first excited state is

$$1s^2 1s^2 [s]^2 [s]^2 [y]^2 [y]^2 [z + z]^2 [x + x][x - x] \text{ singlet and triplet;}$$

$[s]$, $[y]$, $[x]$, and $[z]$ are molecular orbitals built up as linear combinations of those of the $1s$ H and $2s$, $2p_x$, $2p_y$, $2p_z$ C orbitals. In "perpendicular" ethylene, the z orbitals overlap, giving a bond $[z + z]^2$, but the $[x]$ do not. The levels in this case fall very near to each other. The relative term depths calculated indicate that the lowest energy state is planar. It is, however, shown that the excited " planar " state lies higher than, and can intercombine with, a " perpendicular " level. This suggests a mechanism for the photochemical isomerisation of *cis-trans* isomerides.

In a later work Mulliken [67] constructs molecular orbitals for molecules RX_n and discusses the structure, ionisation potentials, and stability of CH_4, NH_3, H_2O, NH_4, CH_3, etc. The structure $1s^2 2[s]^2 2[p]^6$ can be assigned to CH_4 without introducing a hybridisation of s, p orbitals.

C. P. Snow and C. B. Allsopp [68] have discussed the C═C bond and find experimentally that alteration of the symmetry relationships in ethylenic compounds does not materially affect the levels and transitions noticed. Lennard-Jones [69] has examined the structure of simple radicals. The change from O to NH and CH_2, which are isoelectronic, is followed, and similarly $F \longrightarrow HO \longrightarrow NH_2$. The reorganisation of radicals in dissociation processes is also discussed.[70] Hückel [71] has also investigated the electronic arrangements in certain organic free radicals.

In studying the case of methane, J. H. van Vleck [72] has shown mathematically that there is justification for Mulliken's idea that s–p hybridisation does not occur. Slater and Pauling's method of localised bonds avoids excessive electronic accumulation on the same atom, but it is shown by van Vleck that this accumulation can occur. The Slater–Pauling method does not allow the wave functions to be of a symmetry type appropriate to a tetrahedral field.

The above can only be regarded as a rather fragmentary account of a very complicated subject, but it may serve to indicate the general trend of the problems involved. A real understanding of the subject matter can only be gained from a more detailed study of the literature referred to.

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[67] *J. Chem. Physics*, 1933, **1**, 412.

[68, 69, 70, 71] *Trans. Faraday Soc.*, in press.

[72] *J. Chem. Physics*, 1933, **1**, 177, 219.

Little mention can be made of the vibration and rotation levels of molecules; nor can the practical consequences of the interaction of electronic and rotational motion be discussed.* For diatomic molecules the elementary theory has been outlined in previous reports. For polyatomic molecules the levels and their statistical weights are summarised from a theoretical standpoint by D. M. Dennison [73] and examples are given by D. S. Villars.[74] For rotational levels three cases can be distinguished, a collinear molecule, a symmetrical spinning top, and an asymmetric top.

G. Herzberg and E. Teller [75] have discussed the selection rules for vibrational quanta in electronic transitions. Different types of vibration depending on symmetry relationships are distinguished. It is shown that in absorption from the ground state only those bands appear which are associated with the excitation of total-symmetrical vibrations.

Hyperfine Structure and Nuclear Moments.—It is not quite true to say that all the energy of an atom is electronic. In general a quantum number i has to be introduced in addition to n, l, s, j and m, due to the fact that the nucleus spins on its own axis.[76] This nucleus spin has angular momentum $i \,.\, h/2\pi$ and a magnetic moment which interacts with the extranuclear electrons. In terms of the vector model i and j must be compounded quantum-vectorially to give f, the total atomic angular momentum. Thus $f = (j + i)$, $(j + i - 1)$, ... $(j - i)$ or $(i + j)$, $(i + j - 1)$, ... $(i - j)$ according as j or i is the greater, and there will be, instead of each original j level, $(2i + 1)$ or $(2j + 1)$ levels. The interaction energies and relative separation of the levels can be evaluated from the quantum numbers.[77] Their very small magnitude gives the name hyperfine structure. Thus, in the bismuth spectrum the D^2 level splits into four, the $^2D_{\frac{5}{2}}$ into six, the $^2P_{\frac{1}{2}}$ into two, so that $i > \frac{5}{2}$. From the interval relationships the value found is $i = \frac{9}{2}$.[78]

A quite different interpretation of hyperfine structure is, however, possible; this explains the effect as due to the presence of different isotopes. Not the mass, but the actual structural difference of the isotopic nuclei is responsible, giving each isotope a slightly different non-Coulombian field. Though it is not always possible to differentiate spin and isotope effects, the Zeemann effect is helpful.

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[73] *Rev. Mod. Physics*, 1931, **3**, 280.

[74] *Chem. Reviews*, 1932, **9**, 369; cf. Mecke, "Molekülstruktur," p. 23.

[75] *Z. physikal. Chem.*, 1933, [*B*], **21**, 410; *A.*, 766.

[76] W. Pauli, *Naturwiss.*, 1924, **12**, 741.

[77] L. Pauling and S. Goudsmit, "Line Spectra," Chap. XI.

[78] S. Goudsmit and E. Back, *Z. Physik*, 1927, **43**, 254, 321; *A.*, 1927, 706; 1928, **47**, 174; *A.*, 1928, 340.

* Cf. Rabinowitsch, *Z. Elektrochem.*, 1931, **38**, 451; also Jevons, Weizel, *opp. cit.*

In the application of this subject to the investigation of nuclear structure, the magnetic moments of the nuclei and the so-called $g(I)$ factors (ratios of magnetic to mechanical nuclear moment) are important.[79] Measurements of these quantities for different atoms are multiplying very rapidly and it is impossible to list all the results here; i values can be found in Pauling and Goudsmit's book and especially in the report of Kallmann and Schüler.[80] Typical i values are He^4, 0; Li^9, 0; Li^7, $\frac{3}{2}$; Na^{23}, $\frac{5}{2}$; Cl^{35}, $\frac{5}{2}$; Br^{81}, $\frac{3}{2}$; I^{127}, $\frac{9}{2}$. An interesting case is that of lead.[81] In the past year many atoms have been studied, including Cu, Al, In, Ga, Rb, As, Zn, N, Kr, F, Sn, Sb.[81] S. Goudsmit [82] and E. Fermi and E. Segrè [83] have examined hyperfine structure theoretically.

The spin of the proton can be determined from the alternation in intensity of lines in rotation bands in the hydrogen molecular spectrum.[84] As for the electron, the spin $i = \frac{1}{2}$ Bohr units. On this basis it should be possible from observed i values to ascribe nuclear configurations. There is, however, still some doubt whether intranuclear electrons spin, and this must at present be left an open question. A discussion of the facts has been given by H. Schüler and H. Westmeyer,[85] and by N. S. Grace,[86] who concludes that nearly all nuclei with large magnetic and mechanical moments are of odd atomic number, whilst those with small or zero moments are of even atomic number.

Another method can be used to determine the magnetic moments of atoms, even when they are very small.[87] This is the Stern–Gerlach experiment, which involves the splitting of levels in an inhomogeneous magnetic field.[88]

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[79] J. C. McLennan, *Proc. Roy. Soc.*, 1932, **136**, [*A*], 754; *A.*, 1932, 791; G. Gamow, "Atomic Nuclei and Radioactivity," Oxford, 1931, p. 23.

[80] *Ergeb. exakt. Naturwiss.*, 1932, **11**, 134.

[81] R. Ritschl, *Z. Physik*, 1932, **79**, 1; *A.*, 2; G. Breit, *Physical Rev.*, 1932, **42**, 348; A. G. Shenstone and J. J. Livingood, *Physical Rev.*, 1931, **37**, 1023; R. C. Gibbs and P. G. Krüger, *ibid.*, p. 656, 1559; *A.*, 1931, 992; H. E. White, *ibid.*, p. 1175; D. A. Jackson, *Z. Physik*, 1933, **80**, 59; J. S. Campbell, *Physical Rev.*, 1931, **38**, 1906; *Nature*, 1933, **131**, 204; *A.*, 334; D. A. Jackson, *Proc. Roy. Soc.*, 1933, [*A*], **139**, 673; *A.*, 439; M. F. Crawford and A. M. Crooker, *Nature*, 1933, **131**, 655; *A.*, 547; H. Schüler and H. Westmeyer, *Z. Physik*, 1933, **81**, 565; *A.*, 547; R. F. Bacher, *Physical Rev.*, 1933, **43**, 1001; *A.*, 767; H. Kopfermann, *Z. Physik*, 1933, **85**, 353; *A.*, 1095; **83**, 417; *A.*, 880; J. S. Campbell, *ibid.*, **84**, 393; *A.*, 991; S. Tolansky, *Nature*, 1933, **132**, 318; *A.*, 1095; J. S. Badami, *Z. Physik*, 1932, **79**, 206; *A.*, 2.

[82] *Physical Rev.*, 1933, **43**, 636; *A.*, 552.

[83] *Z. Physik*, 1933, **82**, 729; *A.*, 759.

[84] Jevons, "Band Spectra," p. 139; Weizel, "Bandenspektren," p. 140; Kronig, "Band Spectra and Molecular Structure," p. 94.

[85] *Naturwiss.*, 1933, **21**, 674; *A.*, 1101.

[86] *Physical Rev.*, 1933, **44**, 361; *A.*, 1101.

In two papers of fundamental importance, R. Frisch and O. Stern [89] and I. Estermann and Stern [90] have described the measurement of the magnetic moment of the proton. That the mechanical moments of both electron and proton are $\frac{1}{2} \cdot h/2\pi$ was stated above. The magnetic moment of the electron is $2 \cdot \frac{e}{2mc} \cdot \frac{1}{2} \cdot \frac{h}{2\pi}$, a unit Bohr magneton. If similar relationships apply to the proton, its magnetic moment will, by virtue of the different mass, be $\frac{1}{1840}$ times smaller than a Bohr magneton. This has been called a unit nuclear magneton. The hydrogen molecule is peculiarly suitable for a Stern–Gerlach experiment: very low temperatures can be used, giving large deflexions, and the technique of plate development has been well worked out. Moreover, there are the two forms, ortho and para, differing in nuclear spin arrangement. In para-hydrogen the spins are opposed and the nuclei contribute nothing to a magnetic moment. The latter can only arise from a molecular rotation with quantum numbers 0, 2, 4, . . . With ortho-hydrogen the spins are parallel, and in addition to the magnetic moment resulting from the molecular rotation (quantum numbers 1, 3, 5, . . .) there will be a nuclear magnetic moment double that due to a single proton. Two determinations are therefore made. At the temperature of liquid hydrogen, para-hydrogen correctly proves to have no magnetic moment. At somewhat higher temperatures, two quanta of rotation energy are taken up, and from the measured magnetic moment associated with these, that corresponding to one quantum is calculated. At the temperature of liquid hydrogen again, ortho-hydrogen possesses one quantum of rotational energy. If the magnetic moment associated with this is subtracted from the whole measured, the magnetic moment due to the two nuclei follows. The remarkable fact is that the value for a single proton is approximately 2·5 nuclear magnetons. This result is likely to be of profound significance.

In addition the rotational magnetic moment is about one nuclear magneton. This can only be explained if it is assumed that the electron cloud " skids " during the rotation.[91]

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[87] F. Knauer and O. Stern, *Z. Physik*, 1926, **39**, 7808; *A.*, 1927, 92; 1929, **53**, 766; *A.*, 1929, 490; J. B. Taylor, *ibid.*, 1929, **57**, 242.

[88] O. Stern, *ibid.*, 1926, **39**, 751.

[89] *Ibid.*, 1933, **85**, 4; *A.*, 996.

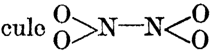
[90] *Ibid.*, p. 17; *A.*, 996.

[91] G. C. Wick, *ibid.*, p. 25; *A.*, 997.

Miscellaneous.—A few matters of a general nature may be mentioned. Very many investigations during the year concern the absorption spectra of polyatomic molecules, but the discussion of these must be postponed. The development of ultra-violet and vacuum spectroscopy technique has led to the study of the spectra of more highly ionised atoms. Typical examples are O^{III}, O^{IV}, O^{V}, Br^{V}, Br^{VI}, Br^{VII}, Mn^{VI}, Fe^{VII}, Co^{VIII}, Ni^{IX}, Rb^{II}, Rb^{III}, Rb^{IV}, Sb^{VI}, etc. As the first of a series of papers compiling critically the data on atomic and molecular spectra of the halogens, W. E. Curtis and S. F. Evans have discussed iodine.[92] Finkelnburg[93] has summarised the facts and interpretations suggested for continuous spectra of gases and vapours. The application of the Franck–Condon principle to the potential-energy curves of molecules underlies the interpretations. W. A. Noyes[94] has outlined the correlations between spectroscopy and chemistry, and Norrish's work on the photochemical decomposition of polyatomic molecules containing in particular the carbonyl group has been continued.[95] D. Chilton and E. Rabinowitsch[96] have measured the absorption spectrum of iodine in the adsorbed state. Mention of O_4 has again been made by some workers.

H. W. T.

Molecular Structure.

The methods of determination of intramolecular distances, angles, and force constants from spectroscopic data have been consolidated during the year. The long-wave rotational absorption spectra of water, ammonia, and phosphine have been examined, leading, in the case of ammonia, to the distances (in Å.U.): $N^-H = 1{\cdot}01$, $H^-H = 1{\cdot}61$.[1] The most important advances have been made in the interpretation of *vibrational* data of molecules (obtained from near infra-red, Raman, and electronic spectra), from which angles and force constants can be evaluated. Measured vibrational frequencies for a simple molecule must first be assigned to specific modes of vibration according to the rules of Placzek and Dennison.[2] The assignment of vibrational frequencies to the molecules of sulphur dioxide and chlorine dioxide shows that their apex angles are both about 120° [3] while that of the molecule chlorine monoxide is probably about 90°.[4] The assignment of the twelve fundamental frequencies of the molecule  ${}^{O}_{O}\!>\!N{-}N\!<\!{}^{O}_{O}$ is discussed by G. B. B. M. Sutherland.[5]

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[92] *Proc. Roy. Soc.*, 1933, **141**, [*A*], 603; *A.*, 1096.

[93] *Physikal. Z.*, 1933, **34**, 529.

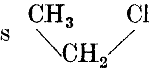
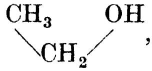
[94] *Rev. Mod. Physics*, 1933, **5**, 280.

[95] *Trans. Faraday Soc.*, in press; *J.*, 1933, 1533.

[96] *Z. physikal. Chem.*, 1932, [*B*], **19**, 107; *A.*, 2.

[1] J. Kühne, *Z. Physik*, 1933, **84**, 722; *A.*, 998; N. Wright and H. M. Randall, *Physical Rev.*, 1933, **44**, 391; H. J. Unger, *ibid.*, **43**, 123; cf. *Ann. Reports*, 1932, **29**, 62.

[2] G. Placzek, *Z. Physik*, 1931, **70**, 84; G. Placzek and E. Teller, *ibid.*, 1933, **81**, 209; D. M. Dennison, *Rev. Mod. Physics*, 1931, 280.

A matter of great moment in work on the vibrations of molecules is the question of the interaction of the vibrational frequencies. Generally, the separate frequencies of different links can be treated as roughly independent and constant. The cyanogen halides, which are linear and have the nitrile structure,[6] form a good example of this, and it has been shown that the four fundamental frequencies of the molecules  and , treated as three-particle systems, do not interact to any great extent.[7] In cases, however, where one fundamental frequency is nearly equal to or is nearly a multiple of another, resonance interaction must be considered, and this subject has received theoretical and experimental investigation.[8] The two symmetrical vibration frequencies of the water molecule are almost equal, and are represented by the absorption band at about 3700 cm.$^{-1}$ (2·7 μ) and the Raman line at 3650 cm.$^{-1}$,[9] while the unsymmetrical frequency appears as the 6·25 μ absorption band. Complete agreement, however, has not yet been reached as to the exact values of the two symmetrical frequencies.[10] Besides the question of resonance, the effects of the deviations of the vibrations from harmonic motion [11] and of the interactions of rotation and vibration are important. In one case, that of the carbon dioxide molecule, where the experimental data are very accurate and extensive, a complete treatment, taking into account all these factors, has been given by A. Adel and D. M. Dennison.[12] They derive an equation containing twelve constants (*viz.*, the three fundamental vibrational frequencies, their anharmonic constants, and rotational constants) which closely describes the behaviour of the molecule up to at least its fifth vibrational level. The anharmonic constants of vibration so determined open up a new line of inquiry, as they form a measure of the interaction of the non-linked atoms (on the older conceptions of valency) of the molecule.

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[3] C. R. Bailey and A. B. D. Cassie, *Proc. Roy. Soc.*, 1933, [*A*], **140**, 605; Z. W. Ku, *Physical Rev.*, 1933, **44**, 376; L. Lotmar, *Z. Physik*, 1933, **83**, 765.

[4] C. R. Bailey and A. B. D. Cassie, *Proc. Roy. Soc.*, 1933, [*A*], **142**, 129.

[5] *Ibid.*, **141**, 342.

[6] W. West and M. Farnsworth, *J. Chem. Physics*, 1933, **1**, 402.

[7] P. C. Cross and J. H. van Vleck, *ibid.*, p. 350; cf. G. Buss, *Z. Physik*, 1933, **82**, 445; O. Eichmann, *ibid.*, p. 461.

[8] J. Horiuti, *ibid.*, **84**, 380; *A.*, 998; W. V. Norris and H. J. Unger, *Physical Rev.*, 1933, **44**, 467; L. Tisza, *Z. Physik*, 1933, **82**, 48.

[9] D. A. Rank, *J. Chem. Physics*, 1933, **1**, 504.

[10] J. H. van Vleck and P. C. Cross, *ibid.*, p. 357; R. Mecke, W. Baumann, and K. Freudenberg, *Z. Physik*, 1933, **81**, 313, 345, 465.

[11] Cf. the case of acetylene; G. B. B. M. Sutherland, *Physical Rev.*, 1933, **43**, 883.

[12] *Ibid.*, p. 716; **44**, 99; E. F. Barker and A. Adel, *ibid.*, **44**, 185; *A.*, 998.

E. J. B.

R. P. Bell.
E. J. Bowen.
C. N. Hinshelwood.
H. W. Thompson.
J. H. Wolfenden.

INORGANIC CHEMISTRY.

1. Atomic Weights.

The striking contribution of mass-spectrum photometry to our knowledge of the atomic weights of the elements forms the subject of F. W. Aston's Liversidge lecture [1] in which the results obtained up to December 1932 are summarised. Of the 35 elements examined, 19 agree within 1 part in 4000 with the chemical values; a correspondence as close perhaps as can be expected in view of the present uncertainty in the proportion of the oxygen isotopes. The remaining elements examined exhibit a concordance of 1 part in 1000 or greater, with the notable exceptions of B, P, Sc, Nb, Ta, Se, Ru, and Os. For all of these the International value exceeds the physical value, varying from 1 part in 200 for ruthenium to 1 part in 780 in the case of phosphorus.

The physical value for boron is admittedly too low on account of the enhanced photographic effect of its lighter isotope, but the discordance of the elements scandium (1 in 320), niobium (1 in 232), and tantalum (1 in 360) calls for further investigation, especially in view of the recent redetermination of the atomic weight of the last metal.[2]

Aston found these elements to be simple, and no indication of higher isotopes was discovered, from which he concluded that the chemical atomic weights were too high. This has since proved to be the case for another element, selenium, which in Aston's table was shown to exceed the photometric estimate by 1 part in 330.

O. Hönigschmid and W. Kapfenberger,[3] after indicating sources of error in the older chemical values, have now linked selenium to silver by the synthesis of silver selenide, a series of closely concordant ratios being obtained which give with Ag = 107·880, Se = 78·962 instead of the older value 79·2 and in close agreement with Aston's figure 78·96. No recent values are available for ruthenium or osmium. The atomic weight of phosphorus calls for revision in view of the close agreement between the value found by M. Ritchie [4] from the limiting density of phosphine and that of Aston.

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[1] *J.*, 1932, 2888.

[2] K. R. Krishnaswami, *J.*, 1930, 1277; *A.*, 1930, 975.

[3] *Z. anorg. Chem.*, 1933, **212**, 198; *A.*, 659.

[4] *Proc. Roy. Soc.*, 1930, [*A*], **128**, 551; *A.*, 1930, 1104.

A full account of the revision of the atomic weight of tellurium [5] has now appeared. From the ratios $TeBr_4$: 4Ag : 4AgBr by the classical methods, Te = 127·61, was obtained whilst a synthesis of silver telluride yielded an identical figure which is 0·1 unit higher than the previously accepted value, but 0·4 unit lower than that obtained with the mass spectrograph by Aston in 1931. That the chemical and physical values now agree is due to K. T. Bainbridge,[6] who succeeded in obtaining a much better mass spectrum of this element which disclosed three new isotopes of lower mass.

During 1933 a number of important papers have been published by Baxter and his co-workers on the atomic weights of arsenic, lead, indium, thallium, potassium, and cæsium. In the light of experience gained with the preparation of various volatile inorganic halides, G. P. Baxter, W. E. Shaeffer, M. J. Dorcas, and E. W. Scripture [7] have prepared in a highly purified state arsenic trichloride and tribromide, and analysed them by the standard method of precipitation with silver followed by nephelometric titration. From the ratios $AsCl_3$: Ag and $AsBr_3$: Ag, a value for arsenic of 74·906 was obtained, distinctly lower than the International value 74·93. In a later paper, Baxter and W. E. Shaeffer [8] published further results from the ratio $AsCl_3$: I_2O_5, which gave mean values for arsenic ranging from 74·906 to 74·916. They concluded that 74·91 was a close approximation for the true value for this element and that J. H. Křepelka's [9] result obtained in 1930 was too high. The new value is now 0·01 unit lower than the physical value 74·92.

In the paper on thallium,[10] Hönigschmid, Birckenbach, and Kothe's value of 204·39 is confirmed by the analysis of thallous chloride, giving the value 204·40 in close conformity with Aston's figure of 204·41, but somewhat higher than the figure of 204·34 found by H. V. A. Briscoe, S. Kikuchi, and J. B. Peel.[10a]

Attention has often been drawn to the discrepancy between the chemical and the physical values for the atomic weight of cæsium. As a rule when there is a divergence the chemical value is the higher. In the case of this element the reverse is true, and the physical value is the greater by 0·1 unit or 1 part in 1330. Now cæsium is a simple element and its packing fraction was measured in 1932 [11] and found to be − 5 ± 2, corresponding to an atomic weight on the chemical scale of 132·917 so that the physical evidence is very strong. This discrepancy has now been explained and a chemical value obtained of 132·91.[12] 1200 G. of the less soluble fractions obtained from the recrystallisation of 4 kg. of cæsium nitrate from the mineral pollucite were recrystallised three times as perchlorate and, after conversion into chloride and fusion, again recrystallised thrice. The arc spectrum showed the absence of potassium and rubidium, and analysis after fusion in platinum in a quartz bottling apparatus gave the value quoted.

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[5] O. Hönigschmid, R. Sachtleben, and K. Wintersberger, *Z. anorg. Chem.*, 1933, **212**, 242; *A.*, 761.

[6] *Physical Rev.*, 1932, [ii], **39**, 1021; *A.*, 1099.

[7] *J. Amer. Chem. Soc.*, 1933, **55**, 1054; *A.*, 442.

[8] *Ibid.*, p. 1957; *A.*, 659.

[9] *Coll. Czech. Chem. Comm.*, 1930, **2**, 255; *A.*, 1930, 975.

[10] G. P. Baxter and J. S. Thomas, *J. Amer. Chem. Soc.*, 1933, **55**, 2384; *A.*, 882.

[10a] *Proc. Roy. Soc.*, 1931, [*A*], **133**, 440; *A.*, 1931, 1348.

[11] F. W. Aston, *Proc. Roy. Soc.*, 1932, [*A*], **134**, 57; *A.*, 1932, 209.

Results obtained with indium [13] by improved methods and with due regard to the solubilities of the silver halides gave concordant values for the ratios $InCl_3 : 3Ag$ and $InBr_3 : 3Ag$; the average figure found gives In = 114·76.

Interest attaches to the determination of the atomic weights of radiogenic leads, especially in view of recent work with the mass spectrograph on ordinary lead and lead extracted from pure specimens of pitchblende and thorite and used in the form of lead tetramethyl. Ordinary lead [14] showed the presence of 5 new isotopes of which 204 was the most abundant. The mean mass number found was 207·190, in close agreement with the accepted chemical value and with new values found independently in America and Germany. No lines corresponding to the new isotopes were found in the uranium and thorium leads. The purest sample of the uranium lead from Katanga consisted entirely of isotopes 206 and 207 in the proportion of 93·3 to 6·7, giving a mean mass number of 206·067. The atomic weights of three uranium leads from the same source have been determined by O. Hönigschmid, R. Sachtleben, and H. Baudrexler,[15] who get values (agreeing within the limits of error) the mean of which is 206·03, in agreement with Aston. Baxter and Alter,[16] however, found from Katanga pitchblende values slightly below 206, and for lead extracted from Bedford cyrtolite [17] (a hard zirconium silicate containing uranium and lead) the lowest recorded figure for uranium lead, *viz.*, 205·92 ± 0·02. It is difficult to believe that this lead can have a value as low as this, for it would indicate a very small percentage of actinium lead, the isotope 207, but since the Baxter and the Hönigschmid value for ordinary lead agree closely, the cause of this divergence is obscure.

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[12] G. P. Baxter and J. S. Thomas, *J. Amer. Chem. Soc.*, 1933, **55**, 858; *A.*, 333.

[13] G. P. Baxter and C. M. Alter, *ibid.*, p. 1943; *A.*, 659.

[14] F. W. Aston, *Proc. Roy. Soc.*, 1934, [*A*], **140**, 535.

[15] *Z. anorg. Chem.*, 1933, **214**, 104; *A.*, 1099.

[16] *J. Amer. Chem. Soc.*, 1933, **55**, 2785; *A.*, 882.

[17] *Ibid.*, p. 1445; *A.*, 550.

Another apparent discrepancy between the results of the American and the German specialists in the determination of atomic weights by classical methods was furnished by the results recently published for potassium by Baxter and W. M. MacNevin,[18] who after a most careful investigation concluded that the true value for this element from the mean of 31 experiments from the ratio KCl : Ag was 39·094 with Cl = 35·457 and Ag = 107·880. This result confirms the older value K = 39·096 obtained in 1907 by Richards and A. Staehler [19] and by Richards and E. Mueller,[20] who analysed respectively the chloride and the bromide, but it is lower by nearly 0·01 unit than the result of Hönigschmid and J. Goubeau,[21] K = 39·104, which was adopted by the German Atomic Weight Commission in their 8th report [22] and agrees with the value obtained by Richards and E. H. Archibald [23] as early as 1903. A little more than a fortnight after the appearance of Baxter's paper, Hönigschmid and Sachtleben [24] reported a new determination of this constant from the ratio KCl : Ag and KBr : Ag, in which, from the mean of 39 very concordant experiments, they deduced the value K = 39·096 with Cl = 35·457 and Ag = 107·880, a value, it is true, differing inappreciably from Baxter's but diverging from their earlier figure by an amount far outside the errors of experiment. Though the authors are convinced of the correctness of the new value, they are unable to explain why the earlier preparations gave the higher result. There seems little doubt now in view of Baxter's results that Richards and his collaborators obtained a figure very near the truth 27 years ago. No doubt this result will lead to a revision of the KNO_3 : KCl ratio measured by E. Zintl and J. Goubeau [25] in 1927, which, like the ratios for potassium chloride and bromide, gave the high value for potassium, but it is disquieting to find that an error has crept into fundamental ratios which were regarded as affording confirmatory evidence of the correctness of the present value for the atomic weight of silver.

It was only in 1929 that the German Atomic Weight Commission [26] concluded that sufficient evidence was available to decide between the two values for this important standard, *viz.*, Ag = 107·871, based on the ratios $LiClO_4$: LiCl : Ag of Richards and H. H.

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[18] *J. Amer. Chem. Soc.*, 1933, **55**, 3185; *A.*, 994.

[19] *Ibid.*, 1907, **29**, 623.

[20] *Ibid.*, p. 639; *A.*, 1907, ii, 615.

[21] *Z. anorg. Chem.*, 1927, **163**, 93; *A.*, 1927, 806.

[22] *Ber.*, 1928, [*B*], **61**, 1.

[23] *Proc. Amer. Acad. Arts Sci.*, 1903, **34**, 373; *A.*, 1903, ii, 366.

[24] *Z. anorg. Chem.*, 1933, **213**, 365; *A.*, 994.

[25] *Ibid.*, 1927, **163**, 302; *A.*, 1927, 806.

[26] *Ber.*, 1929, **62**, 1.

Willard,[27] and Ag = 107·879 obtained by Richards and G. S. Forbes[28] by the synthesis of silver nitrate.

This small difference of 1 part in 10,000 caused a much greater uncertainty in the values of a number of elements. Thanks chiefly to the work of the Munich school, it was found possible to decide in favour of the higher figure, and the Commission based their decision mainly on two investigations : (1) the reduction of the purest silver nitrate to silver by hydrogen, and (2) the analysis[29] of barium perchlorate and barium chloride which links silver to oxygen by the ratios $BaClO_4 : BaCl_2 : Ag$. The first research, carried out with an exceptionally fine technique, yielded for the analysis of silver nitrate a mean value for the ratio $AgNO_3 : Ag$ of 1·57479, identical to the last place of decimals with the synthesis of the same salt carried out 18 years before by Richards and Forbes,[28] and gave with N = 14·008, Ag = 107·879. The second method yielded values for silver varying only from 107·877 to 107·882. Confirmatory evidence was afforded by a number of less direct ratios, among which may be mentioned $NaNO_3 : NaCl : Ag$,[30] the corresponding potassium ratios, as well as the ratio $2Ag : SO_2 : Ag_2SO_4 : AgCl$,[31] so that at the present time very strong evidence is available that the uncertainty in this important sub-standard does not exceed at most a few units in the third place of decimals, an accuracy much greater than anything achieved so far by mass-spectrographic methods. Many investigations of a similar character using every modern refinement have in recent years been carried out at Munich ; mention should be made of a revision of the atomic weight of chlorine by two syntheses[32, 33] of silver chloride which confirmed Richards's value 35·457, which, in turn, is only 0·001 unit lower than the most probable value for this element calculated from physicochemical measurements by Moles.[34] The synthesis of silver sulphide,[35] linking the two elements and giving S = 32·066 in conformity with the older values of F. P. Burt and F. L. Usher[36] and of Richards and G. Jones,[37] and the determination of the atomic weights of calcium,[38] erbium,[39] ytterbium,[40] and iodine[41] are important contributions from this laboratory.

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[27] *Z. anorg. Chem.*, 1910, **66**, 229; *A.*, 1910, ii, 292.

[28] *Ibid.*, 1907, **55**, 34; *A.*, 1907, ii, 685.

[29] O. Hönigschmid and R. Sachtleben, *ibid.*, 1929, **178**, 1; *A.*, 1929, 370.

[30] E. Zintl and A. Meuwsen, *ibid.*, 1924, **136**, 223; *A.*, 1924, ii, 608.

[31] O. Scheuer, *Arch. Sci. phys. nat.*, 1913, **36**, 381.

[32] O. Hönigschmid and S. B. Chan, *Z. anorg. Chem.*, 1927, **163**, 315; *A.*, 1927, 806; also *J. Amer. Chem. Soc.*, 1931, **53**, 3012.

[33] O. Hönigschmid and L. Birkenbach, *Z. anorg. Chem.*, 1927, **163**, 315; *A.* 1927, 806.

[34] *Z. physikal. Chem.*, 1925, **115**, 61; *A.*, 1925, ii, 346.

[35] O. Hönigschmid and R. Sachtleben, *Z. anorg. Chem.*, 1931, **195**, 207; *A.*, 1931, 279.

[36] *Proc. Roy. Soc.*, 1911, **85**, 82; *A.*, 1911, ii, 389.

[37] *J. Amer. Chem. Soc.*, 1907, **29**, 825; *A.*, 1907, ii, 685.

The question of the exact value for nitrogen is of importance in calculating the atomic weight of silver. This was discussed in 1927 by Moles,[42] who carried out an elaborate research on the density of the gas and obtained the value 14·0082, and the very careful work of Baxter and H. W. Starkweather[43] leads to an almost identical figure. Since then the attempt has been made to deduce the atomic weight of this element from the limiting densities of nitrous oxide[44] and ammonia,[45] but it is doubtful whether it is possible to obtain results of the highest accuracy yet from physicochemical measurements with condensable gases.

A gravimetric synthesis of ammonium chloride and ammonium bromide was carried out in 1931 by Baxter and C. H. Greene.[46] Gaseous ammonia was weighed condensed on cooled chabazite, allowed to evaporate into solutions of hydrogen chloride and bromide until these were neutral, and the halide then compared with silver. The ratio Ag : NH_3 was then measured and from these results N = 14·0078 or 14·0080 according as Ag = 107·879 or Ag = 107·880.

In recent years the determination of the limiting densities of gases as a method of determining the exact atomic weights of a number of elements has come into prominence. Suggested originally by D. Berthelot and Lord Rayleigh, it was used by Guye and the Geneva school to check and control results obtained by purely chemical means, and with its help valuable independent data for the atomic weights of nitrogen, chlorine, bromine, sulphur, and carbon were obtained.

The application of this principle is strongly advocated by Moles, who, in addition to the work on nitrogen, has recently with L. R. Pire[47] and later with M. T. Salazar[48] revised the density of carbon monoxide and obtained a value for carbon = 12·006. The admirable work, too, of Baxter and Starkweather on the densities of helium, neon, argon, nitrogen, and oxygen at a series of pressures has extended the accuracy of the standard methods of weighing gases to very fine limits.

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[38] O. Hönigschmid and K. Kempter, *Z. anorg. Chem.*, 1931, **195**, 1; *A.*, 1931, 279.

[39] O. Hönigschmid and W. Kapfenberger, *ibid.*, 1933, **214**, 97; *A.*, 1099.

[40] O. Hönigschmid and H. Striebel, *ibid.*, 1933, **212**, 385; *A.*, 762.

[41] *Idem*, *Z. physikal. Chem.*, Bodenstein Festband, 1931, 282; *A.*, 1931, 1208; *Z. anorg. Chem.*, 1932, **208**, 53.

[42] *Ibid.*, 1927, **167**, 49; *A.*, 1927, 1120.

[43] *Proc. Nat. Acad. Sci.*, 1926, **12**, 703; *A.*, 1927, 194.

[44] T. Batuecas, *Z. physikal. Chem.*, Bodenstein Festband, 1931, 18; *J. Chim. physique*, 1931, **28**, 572; *A.*, 1931, 1222.

[45] E. Moles and T. Batuecas, *Anal. Fis. Quim.*, 1930, **28**, 87; *A.*, 1930, 1357.

[46] *J. Amer. Chem. Soc.*, 1931, **53**, 604; *A.*, 1931, 407.

[47] *Anal. Fis. Quim.*, 1929, **27**, 267; *A.*, 1929, 873.

[48] *Ibid.*, 1932, **30**, 182; *A.*, 1932, 566.

Unless the densities of gases can be compared at very low pressures, which cannot be done at present with the requisite degree of accuracy, a knowledge of the compressibility is necessary, and the accurate determination of this factor from 1 atmosphere down to low pressures presents many difficulties, especially when, as is the case with the liquefiable gases, the factor is large and extrapolation to zero pressure uncertain. Recent work on the compressibilities determined by the usual methods is contained in a paper by Batuecas, C. Schlatter, and G. Maverick,[49] where a study of the gases nitrogen, carbon monoxide, ammonia, hydrogen chloride, and hydrogen sulphide is reported. W. Cawood and H. S. Patterson [50] have recently made a study of the PV–P isothermals of a series of gases over a pressure range of from 1 to 3 atmospheres, and they find, even with gases like carbon dioxide and sulphur dioxide, no indication of curvature. They contend that the low-pressure isothermals used in calculating the limiting densities are straight lines to within small limits (1 part in 5000) and there is much evidence from high-pressure data [51] and from modern gas equations such as the Beattie–Bridgman equation to support this. If this is so, the problem of measuring the limiting densities of liquefiable gases is simplified, though the effects of adsorption at low pressures will need careful study.

The same investigators [52] have redetermined the meniscus corrections to be applied to mercury surfaces in glass tubes of varying diameter, and have obtained data of great value for correcting manometric readings when the highest accuracy is necessary. Another important error which may amount to 0·05 mm. is that caused by irregular refraction, and it is shown how this may be reduced to a minimum by constructing the manometer of very thin-walled tubing.

An alternative procedure for comparing the densities of gases is by means of the quartz micro-displacement balance, a method which has many advantages. It has been applied to find the atomic weights of xenon,[53] krypton,[54] of fluorine [55] from methyl fluoride,

[49] *J. Chim. physique*, 1930, **27**, 45; *A.*, 1930, 283.

[50] *J.*, 1933, 619.

[51] W. Wild, *Phil. Mag.*, 1931, **12**, 41; *A.*, 1931, 899.

[52] *Trans. Faraday Soc.*, 1933, **29**, 514; *A.*, 367.

[53] Patterson and Cawood, *Proc. Roy. Soc.*, 1931, [*A*], **134**, 7; *A.*, 1932, 106.

[54] H. E. Watson, *Nature*, 1931, **127**, 631; *A.*, 1931, 666.

[55] Cawood and Patterson, *J.*, 1932, 2180.

and of carbon.[56] The case of carbon is of interest because the chemical atomic weight must be greater than the value obtained by the mass-spectrograph, which does not take account of the higher isotope C^{13}, but at present it is actually lower, C = 12·00 as against C = 12·001 or 12·0023 according to which factor is used to convert the physical to the chemical scale. The results obtained from a comparison of the densities of carbon monoxide and oxygen at a series of pressures gave 12·011 for the atomic weight of this element, in conformity with the latest measurement of the abundance ratio $C^{12} : C^{13}$ made by F. A. Jenkins and L. S. Ornstein [57] by band-spectrum methods. It appears as if the higher isotope is present to the extent of 1%, and that the atomic weight is close to 12·01, though if this is true it is difficult to understand why some line involving C^{13} has not been detected with the mass spectrograph.

Ever since the discovery that the majority of the chemical elements are mixtures of isotopes, evidence has been accumulating that no difference in isotopic composition is found in specimens of the same element from various sources. The chemical atomic weights are still to be regarded as natural constants. The work on potassium, already quoted, again supports this view for, although both Baxter and Hönigschmid extracted their material from various sources and each compared the potassium salts of vegetable origin with those extracted from minerals, yet no difference in the equivalent was detected. The less volatile potassium, however, obtained by ideal distillation by von Hevesy gave the value 39·109, 0·013 unit above the new figure. Baxter calculates the percentage of K^{41} to be 6·6 in ordinary potassium and 7·3 in the heavier specimen.

Products of radioactive disintegration are, of course, in a different category, and it is of interest to note that again a difference in the atomic weight of calcium [58, 59, 60] in samples from different sources has been reported. This calcium of a higher atomic weight is supposed to originate from K^{41} by a β-ray change.

R. W.-G.

2. New Compounds.

For many years it was supposed that no compound of oxygen and fluorine could exist. In 1927,[1] however, P. Lebeau and A. Damiens demonstrated that oxygen difluoride, OF_2, was produced when water was present in the electrolysis of molten acid potassium fluoride below 100°. It was found later that the oxide was best obtained by passing fluorine in a fine stream through dilute aqueous sodium hydroxide. Now O. Ruff and W. Menzel [2] have isolated a new oxide from the two elements. In their experiments, an equimolecular mixture of oxygen and fluorine at 15—20 mm. pressure was introduced into a quartz container immersed in liquid air and equipped with two electrodes 12 cm. apart. An electric discharge caused the formation of O_2F_2 as a yellow solid, m. p. *ca.* $-160°$. Gaseous O_2F_2 is brown, and above $-100°$ decomposes into OF, a colourless gas of very low boiling and freezing point, which does not re-form O_2F_2 on cooling; OF reacts with HI as follows: $OF + 3HI = 3I + HF + H_2O$. Various electronic structures might be proposed for the molecule O_2F_2. Ruff and Menzel suggest the constitution $O{=}O{=}F_2$ which would be rewritten in modern nomenclature as $O{\leftarrow}O{\leftarrow}F_2$. They do not, however, indicate what they consider the structure of OF to be, beyond remarking that it must be substantially different from that of O_2F_2 since they have not succeeded in re-forming O_2F_2 from OF.

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[56] M. Woodhead and R. Whytlaw-Gray, *J.*, 1933, 846; *A.*, 894.

[57] *Proc. K. Akad. Wetensch. Amsterdam*, 1932, **35**, 1212; *A.*, 333.

[58] J. Kendall, W. W. Smith, and T. Tait, *Nature*, 1933, **131**, 688.

[59] A. V. Frost and O. Frost, *ibid.*, 1930, **125**, 48; *A.*, 1930, 130.

[60] Hönigschmid and Kempter, *loc. cit.*, ref. (38).

[1] *Compt. rend.*, 1927, **185**, 652; *A.*, 1927, 1044.

Another interesting oxide which has recently been prepared is sulphur monoxide. Its existence has frequently been postulated in the Wackenroder reaction and in the genesis of polythionic acids. This monoxide is produced [3] by an electric discharge in sulphur dioxide or, better, in a mixture of sulphur dioxide and sulphur vapour, at low pressures. Nearly pure SO has been isolated under suitable experimental conditions. At room temperature the oxide is a gas which may be kept for some days in dry vessels. Organic substances (such as tap grease) and water vapour [4] aid decomposition. The rate of decomposition is favoured by rise of temperature, and at 180° it is almost completely decomposed in a minute. Oxygen and the new oxide do not react at room temperature, but they unite when electrically sparked. Aqueous alkalis form a reducing liquid with the monoxide which decolorises indigo and may be described as a solution of sulphoxylate or hydrosulphite. Sulphur monoxide reacts vigorously with metals, forming sulphides. When cooled in liquid air, it gives a red condensate which behaves in a remarkable way on evaporation, for it decomposes completely with the separation of sulphur and the production of sulphur dioxide. The ready spectroscopic detection of the monoxide has indicated that it is one of the products of the reaction between thionyl chloride vapour and certain metals [5] such as silver, sodium, and magnesium, but this method is unsuitable for its preparation. The monoxide was not detected in the reaction between hydrogen sulphide and sulphur dioxide or in the decomposition of either sodium hydrosulphite or sodium thiosulphate.

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[2] *Z. anorg. Chem.*, 1933, **211**, 204; *A.*, 476.

[3] P. W. Schenk, *Z. anorg. Chem.*, 1933, **211**, 150; *A.*, 475.

[4] H. Cordes and P. W. Schenk, *Z. Elektrochem.*, 1933, **39**, 594; *A.*, 1021.

[5] E. Gruner, *Z. anorg. Chem.*, 1933, **212**, 393; *A.*, 795; P. W. Schenk and H. Platz, *ibid.*, **215**, 113.

K. G. Denbigh and R. Whytlaw-Gray[6] have made a valuable observation in fractionally subliming solid sulphur hexafluoride at low temperatures. As fractionation proceeded, the vapour density rose rapidly from *ca.* 73 (that of SF_6) to *ca.* 125, at which it remained steady. They conclude that a new gas S_2F_{10} (M, 254) is probably present with a boiling point in the vicinity of 0°. There are indications of other homologues of sulphur hexafluoride.

A new hexafluoride has recently been prepared. O. Ruff and W. Kwasnik (with E. Ascher)[7] report that by heating rhenium in a current of fluorine at 125° the hexafluoride is formed as a colourless gas which solidifies to light yellow crystals, m. p. 26·4°. From the position of rhenium in the periodic table, a fluoride between WF_6 and OsF_8 would be expected, but these investigators have so far not obtained evidence of it. Previous experiments on the nature of the rhenium chlorides have shown that more than one compound is formed when chlorine is passed over the metal. This is clearly demonstrated by the results of O. Hönigschmid and R. Sachtleben[8] when they attempted to determine the atomic weight of rhenium by the analysis of the chloride. They found the best preparations to be mixtures, since the proportions of rhenium to chlorine were not constant and led in the more reproducible cases to the empirical formula $ReCl_{4\cdot3}$. They also observed that this substance decomposed on heating in an atmosphere of nitrogen with the formation of a less volatile product, whereas similar treatment in the presence of chlorine resulted in complete volatilisation without apparent change. These results are particularly interesting in view of the discovery of a pentachloride of rhenium. So far the highest chloride to be identified is $ReCl_4$,[9] but it is now found that when chlorine reacts with rhenium, the pentachloride can be produced[10] and obtained pure by sublimation in a high vacuum at 200°. This chloride is very sensitive to moisture, and with concentrated hydrochloric acid, chlorine is evolved and H_2ReCl_6 is formed. Dilute hydrochloric acid forms with the chloride a mixture of H_2ReCl_6 and $HReO_4$. Heated in dry nitrogen, the pentachloride yields the trichloride and an equivalent amount of chlorine. The trichloride, which can be purified by sublimation in a vacuum at 500—550°, forms reddish-black lustrous crystals, apparently trigonal, which are only slightly ionised in aqueous solution.[11] This recent work will possibly modify the conclusions which D. M. Yost and G. O. Shull [12] drew from their vapour-density data on the rhenium chlorides.

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[6] *Nature*, 1933, **131**, 763; *A.*, 684.

[7] *Z. anorg. Chem.*, 1932, **209**, 113; *A.*, 40.

[8] *Ibid.*, 1930, **191**, 309; *A.*, 1930, 1338.

[9] H. V. A. Briscoe, P. L. Robinson, and L. M. Stoddart, *J.*, 1931, 2263; *A.*, 1931, 1255.

[10] W. Geilmann, F. W. Wrigge, and W. Biltz, *Angew. Chem.*, 1933, **46**, 223.

Hydrides of silver, copper, gold, beryllium, gallium, indium, and tantalum are formed by the action of atomic hydrogen on the solid element,[13] and a number of most interesting products have been prepared from reactions involving atomic hydrogen at low temperatures. Atoms of hydrogen produced in a discharge at a pressure of 0·5 mm. of mercury rarely react at room or higher temperatures to give addition products, but at the temperature of liquid air or liquid hydrogen such reactions are realisable. K. H. Geib and P. Harteck [14] state that at the temperature of liquid hydrogen it is possible to obtain 100% yields of hydrogen peroxide by the addition of atomic hydrogen to molecular oxygen. They consider that this is not the normal form of the substance but that it reverts to the usual form on warming to – 115°, at which temperature there is some decomposition into water and oxygen, accompanied by considerable foaming. A solid substance containing 70% HgH is produced from the reaction of mercury vapour with hydrogen atoms at low temperatures.

P. Harteck [15] finds that when nitric oxide is passed, at liquid-air temperature, into a stream of hydrogen at 0·5 mm. pressure, split into atomic hydrogen to the extent of 60%, a pale yellow translucent deposit is obtained. This has the empirical formula HNO and proves to be mainly hyponitrous acid with some nitroamine. The same product is obtained from ammonia and oxygen atoms. Although under special conditions hyponitrous acid can be synthesised from hydrogen and nitric oxide, apparently sodium hyponitrite is not formed when nitric oxide reacts with sodium dissolved in liquid ammonia at – 50°. This reaction is well known but doubt has frequently been expressed as to whether the product is really sodium hyponitrite. An investigation by E. Zintl and A. Harder [16] seems to settle this point, for not only does the sodium nitrosyl, $(NaNO)_n$, prove to have different chemical properties from those of sodium hyponitrite but Debye–Scherrer diagrams show that they are quite different. Evidently the nitric oxide molecules are co-ordinated with the sodium in a similar way to carbon monoxide molecules when this gas is passed into a solution of the alkali metals in liquid ammonia at − 50° to give the carbonyls NaCO, LiCO, etc.[17]

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[11] *Idem, Nach. Ges. Wiss. Göttingen*, Math.-phys. Kl., 1932, 579; *A.*, 1130.

[12] *J. Amer. Chem. Soc.*, 1932, **54**, 4657; *A.*, 218.

[13] E. Pietsch (with F. Seuferling, W. Roman, and H. Lehl), *Z. Elektrochem.*, 1933, **39**, 577; *A.*, 1020.

[14] *Ber.*, 1932, **65**, [*B*], 1551; *A.*, 1932, 1098.

[15] *Ber.*, 1933, **66**, [*B*], 423; *A.*, 361.

[16] *Ibid.*, p. 760; *A.*, 578.

W. W.

3. STRUCTURES, ETC.

J. R. Partington and C. C. Shah [18] report that molecular-weight determinations on benzene solutions of ethyl, propyl, butyl, and benzyl esters of hyponitrous acid indicate the formula $R_2N_2O_2$ in accordance with accepted practice. They have also studied the decomposition of the alkaline-earth hyponitrites and noted that on heating they give chiefly the monoxide of the metal, nitrogen, and nitrous oxide, together with some nitrate, nitrite, and nitric oxide.

T. G. Pearson and P. L. Robinson [19] have measured the density and surface tension of pure sulphur hexafluoride, provided by Whytlaw-Gray, and infer from the derived parachor that the octet valency rule is maintained in this compound and that two of the fluorine atoms are attached to the sulphur atom by covalent linkages and the remaining four by semipolar singlet bonds, a possibility suggested by S. Sugden.[20] They maintain that the parachors of selenium and tellurium hexafluorides reveal a similar structure for these compounds. It is very difficult to accept such a constitution for sulphur hexafluoride, for it does not accord with the known chemical properties of the substance, and moreover, as N. V. Sidgwick [21] has emphasised, the meaning of the results from parachor measurements is at present often obscure. In particular, the effects of changes of valency and covalency do not seem to be understood. This opinion seems to be justified, for L. O. Brockway and L. Pauling [22] arrive at a fundamentally different conclusion from their examination of the structures of these hexafluorides by the electron-diffraction method. The diffraction patterns obtained give the following separations (in Å.U.):

S–F, 1·58 ± 0·03; Se–F, 1·70 ± 0·03; Te–F, 1·84 ± 0·03.

These values for the interatomic distances agree very well with those expected for an ionic structure. The sums of the ionic radii are 1·65, 1·78, and 1·92 Å.U. respectively, and these sums are expected to be somewhat larger than the equilibrium distances between small highly charged cations and large anions. The differences 0·07, 0·08, and 0·08 Å.U. are very close to that between the observed Si–F distance 1·68 ± 0·02 Å.U. in the crystal of ammonium silicofluoride and the ionic radius sum 1·77 Å.U. Brockway and Pauling conclude that the structures are ionic, and the fluoride ions are situated at the corners of an octahedron about the appropriate central atom.

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[17] T. G. Pearson, *Nature*, 1933, **131**, 166; *A.*, 238.

[18] *J.*, 1932, 2589.

[19] *J.*, 1933, 1427.

[20] "Parachor and Valency," London, 1930, p. 136.

[21] "The Covalent Link in Chemistry," 1933, p. 94.

[22] *Proc. Nat. Acad. Sci.*, 1933, **19**, 68; *A.*, 341.

Doubt has always existed as to the correct representation of hypophosphoric acid and its salts. This acid is readily formulated as $H_4P_2O_6$, but as H_2PO_3 it is an anomalous compound of phosphorus, with the possible structure $O\leftarrow P(OH)_2$. There is considerable evidence in favour of the double formula, but the molecular weights in solution for the esters, determined by A. Rosenheim and M. Pritze in 1908,[23] indicated the constitution R_2PO_3. Recently, however, A. E. Arbusov and B. A. Arbusov [24] prepared some pure ethyl hypophosphate by the reaction of bromine on sodium diethyl phosphite, $(EtO)_2P{\cdot}ONa$, and found that it gave a molecular weight in accordance with the formula $Et_4P_2O_6$. Moreover, they proved that the pure ester could not be obtained from the alkyl halide and silver hypophosphate, the method used by Rosenheim and Pritze, whose molecular-weight determinations are thereby invalidated. Further support for the double formula has been obtained from magnetic susceptibility measurements.

In general, atoms or ions which contain completed sub-groups possess zero or very small magnetic moments and are diamagnetic, whilst those in which the sub-group is incompletely filled are paramagnetic. On this basis, since H_2PO_3 is an " odd " molecule and $H_4P_2O_6$ is not, it follows that if the hypophosphates have the simpler structure they should be paramagnetic. F. Bell and S. Sugden [25] have therefore determined the magnetic susceptibilities of $Na_2H_2P_2O_6$ (and with $6H_2O$), $Ag_4P_2O_6$, and $(CN_3H_5)_4H_4P_2O_6,2H_2O$, and find them all diamagnetic in accordance with this constitution. They also showed that the products from alkyl halides and silver hypophosphate did not give the reactions of true hypophosphates, confirming the conclusions of Arbusov and Arbusov. Recently, P. Nylen and O. Stelling [26] concluded that the cryoscopic measurements on aqueous solutions of the acid and its sodium salt support the formula $H_4P_2O_6$. Moreover, X-ray examination of the sodium and the barium salt shows only one K-absorption edge corresponding with that expected for the structure $R_4(O_3P{\cdot}PO_3)$.

In spite of numerous investigations, the problem of the constitution of the perchromic acids remains unsolved. It will be recalled that earlier[27] workers considered the red perchromates to be M_3CrO_8, where chromium is septavalent, whilst the blue salts were thought to be $MCrO_5$, with sexavalent chromium. The latter sometimes contained a molecule of hydrogen peroxide of crystallisation. Later, different views were expressed on this matter, and in recent years K. Gleu[28] has maintained that the red perchromates should be formulated as the co-ordination compounds $M_3[Cr(O_2)_4]$ containing quinquevalent chromium, whilst A. Rosenheim and his collaborators[29] suggest the inset constitution where the chromium is sexavalent. R. Schwarz and H. Giese[30] have now degraded potassium perchromate in a tensimeter at 0° and shown that no stoicheiometric relationship exists between the loss of water and oxygen, thus excluding the formula $KCrO_5,H_2O_2$. Moreover, analyses of the very unstable thallous perchromate indicate the formula $TlCrO_6$, whence the potassium salt should be $KCrO_6,H_2O$. Addition of the blue perchromate to excess of acidified potassium permanganate containing a trace of ammonium molybdate and titration of the excess shows the presence of five [O·O] groups in the molecule thus leading to the constitution

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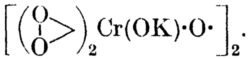
[23] *Ber.*, 1908, **41**, 2708.

[24] *J. pr. Chem.*, 1931, **130**, 121; *A.*, 1931, 1268.

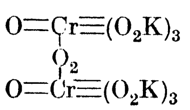
[25] *J.*, 1933, 48; *A.*, 212.

[26] *Z. anorg. Chem.*, 1933, **212**, 169; *A.*, 664.



$$\left[\left(\begin{matrix}O\\|\\O\end{matrix}\!>\right)_2 Cr(OK)\cdot O\cdot\right]_2.$$

Similar treatment of the red perchromate demonstrates that $3\frac{1}{2}$ [O·O] groups are present to each chromium atom, which is fully in accordance with the formula proposed by Rosenheim and his collaborators. Nevertheless, B. T. Tjabbes[31] contends that the magnetic susceptibility of K_3CrO_8 indicates a valency of 5 or 7 for the chromium, and that the value 5 is supported by electronic considerations, isomorphism with the perniobates and pertantalates containing quinquevalent niobium and tantalum, and analogy with the magnetic properties of other compounds of quinquevalent chromium. At present, therefore, there is not general agreement as to the constitution of the perchromates.



$$\begin{matrix}O{=}Cr{\equiv}(O_2K)_3\\ |\\ O_2\\ |\\ O{=}Cr{\equiv}(O_2K)_3\end{matrix}$$

It has long been known that alkaline oxidation of potassium hydroxylaminedisulphonate, $HO{\cdot}N(SO_3K)_2$, gives a solution similar in colour to permanganate from which, on evaporation, yellow crystals are deposited with the empirical formula $ON(SO_3K)_2$. When these crystals are dissolved in water they yield the deep purple solution again. The relationship between the two coloured forms of this compound has always been obscure, but recently

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[27] Ephraim, " Inorganic Chemistry," 1926, p. 419.

[28] *Z. anorg. Chem.*, 1931, **204**, 67.

[29] *Ibid.*, 1932, **209**, 175.

[30] *Ber.*, 1933, **66**, [*B*], 310; *A.*, 241.

[31] *Z. anorg. Chem.*, 1933, **210**, 385; *A.*, **449.**

R. W. Asmussen [32] has shown that the yellow solid has only a feeble paramagnetism whilst the aqueous solution gives nearly the theoretical paramagnetism for an " odd " molecule. These results are suitably interpreted as indicating the equilibrium, solid $[ON(SO_3K)_2]_2 \rightleftharpoons 2(KSO_3)_2NO$, where $(KSO_3)_2NO$ is an " odd " molecule according to the electronic theory of valency. It is interesting to learn that the *X*-ray diagram of the supposed mercurous oxide Hg_2O,[33] prepared by different methods, shows only interferences characteristic of mercuric oxide with some diffuse blackening due to mercury. The investigators remark that no satisfactory evidence of the existence of Hg_2O has yet been produced. In the previous Report attention was directed to the announcement of the isolation of compounds of krypton with chlorine and bromine.[34] It is now proved that the red compound stated to be krypton chloride contains no krypton,[35] and other investigators [36] record negative results in attempts to combine the rare gases with the halogens. Nevertheless, L. Pauling [37] predicts the isolation, in due course, of KrF_6 and XeF_6, with XeF_8 as an unstable compound. Finally, it may be mentioned that L. Pauling and L. O. Brockway [38] conclude from electron diffraction experiments with carbon suboxide, that the molecule is linear. This is in accordance with the usual formulation. The interatomic distances are $C{-}O = 1{\cdot}20 \pm 0{\cdot}02$, $C{-}C = 1{\cdot}30 \pm 0{\cdot}02$ Å.U. These values are intermediate between those expected for triple and double bonds, and the normal state of the molecule may be represented conveniently by the formula $O\underset{\cdots}{=}C\underset{\cdots}{=}C\underset{\cdots}{=}C\underset{\cdots}{=}O$.

W. W.

4. CO-ORDINATION COMPOUNDS.

Modern physics has already provided a secure foundation for the principles which Werner first outlined in his co-ordination theory, and the outstanding feature of present-day researches on this theory is the increasing utilisation of physical methods.

L. Pauling [1] has recently made some striking observations on co-ordination compounds in which the central atom is exhibiting its maximum valency and is associated with the units oxygen, hydroxyl, or water. These units are attracted by the strong central field of a small cation, and the configuration of maximum stability is reached when they are as close to it as possible. If the ions are considered as rigid spheres, then four anions at the corners of a tetrahedron are in contact with a cation at the centre when the ratio ρ of cation radius to anion radius is 0·225. If the ratio be smaller, three anions in contact with the cation prevent a fourth from approaching to within the same distance of the cation, and the arrangement with co-ordination number 4 becomes less stable than with co-ordination number 3 (triangular arrangement). Pauling deduces that the tetrahedron is stable only for $\rho = 0{\cdot}225$ to $0{\cdot}414$; the octahedron (co-ordination number 6) for $\rho = 0{\cdot}414$ to $0{\cdot}713$, and the cube (co-ordination number 8) where ρ is above this. The ionic radii used in these considerations are the "univalent radii"[2] which represent the relative extensions in space of the outer electron shells of the ions.

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[32] *Z. anorg. Chem.*, 1933, **212**, 317.

[33] R. Fricke and P. Ackermann, *ibid.*, **211**, 233; *A.*, 579.

[34] A. von Antropoff, H. Franz, and H. Westerhoff, *Naturwiss.*, 1932, **20**, 688; *A.*, 1932, 566.

[35] A. von Antropoff, H. Frauenhof, and K. H. Krüger, *ibid.*, 1933, **21**, 315; *A.*, 579.

[36] H. Käding and N. Riehl, *ibid.*, p. 479; *A.*, 776; D. M. Yost and A. L. Kaye, *J. Amer. Chem. Soc.*, 1933, **55**, 3390; *A.*, 1128; O. Ruff and W. Menzel, *Z. anorg. Chem.*, 1933, **213**, 206; *A.*, 914.

[37] *J. Amer. Chem. Soc.*, 1933, **55**, 1895; *A.*, 664.

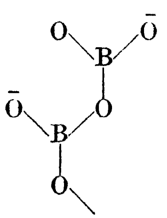
[38] *Proc. Nat. Acad. Sci.*, 1933, **19**, 800.

[1] *J. Amer. Chem. Soc.*, 1933, **55**, 1895; *A.*, 664.

Ratios of Univalent Radii : Cation/Oxygen.

Be^{++}	B^{3+}	C^{4+}	N^{5+}		RO_3 *Region.*	
0·25	0·20	0·17	0·14			
Mg^{++}	Al^{3+}	Si^{4+}	P^{5+}	S^{6+}	Cl^{7+}	
0·48	0·41	0·37	0·34	0·31	0·28	
					RO_4 *Region.*	
Zn^{++}	Ga^{3+}	Ge^{4+}	As^{5+}	Se^{6+}	Br^{7+}	Kr^{8+}
0·50	0·46	0·43	0·40	0·37	0·35	0·33
Cd^{++}	In^{3+}	Sn^{4+}	Sb^{5+}	Te^{6+}	I^{7+}	Xe^{8+}
0·65	0·59	0·55	0·51	0·47	0·44	0·42
					RO_6 *Region.*	

Reference to the above table indicates that the values for boron, carbon, and nitrogen are less than 0·225 in accordance with the existence of H_3BO_3, H_2CO_3, and HNO_3. The value for boron is not far below that required for a co-ordination number 4, so that possibly some metaborates may be salts of $HB(OH)_4$. Metaborates which are usually written as derivatives of HBO_2 are in reality salts of the polymerised acid $(HBO_2)_x$, in which each boron atom is surrounded by three oxygen atoms as in H_3BO_3 (see inset). The *X*-ray study[3] of $Ca(BO_2)_2$ shows this. In this compound each boron is



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[2] L. Pauling, *J. Amer. Chem. Soc.*, 1927, **49**, 765; *A.*, 1927, 399.

[3] W. H. Zachariasen, *Proc. Nat. Acad. Sci.*, 1931, **17**, 617; *A.*, 1932, 114; W. H. Zachariasen and G. E. Ziegler, *Z. Krist.*, 1932, **83**, 354; *A.*, 1933, 13.

surrounded by three oxygen atoms, in a plane. The existence of the tetrahedral hydrate $[Be(H_2O)_4]^{++}$ in $Be(H_2O)_4SO_4$[4] confirms the co-ordination number demanded by the value for beryllium. Salts of acids with formulæ usually written as H_2SiO_3 and HPO_3 are actually polymerised in such a way as to retain the tetrahedral arrangement of four oxygen atoms round the silicon and phosphorus. The prediction[5] that aluminium should occur with co-ordination number 4 as well as 6 has been verified by the examination of many crystals including mica, sodalite, etc. The radius ratio for I^{7+} is not far above the tetrahedron–octahedron transition value. Salts of periodic acid, such as KIO_4, containing a tetrahedral IO_4' ion, are known, but confirmation is still lacking of an octahedral configuration for the acid and salts represented by the formulæ $H_5[IO_6]$, $Ag_5[IO_6]$, $K_2H_3[IO_6]$, etc. Telluric acid is generally recognised as H_6TeO_6 or $Te(OH)_6$ rather than $H_2TeO_4,2H_2O$, and *X*-ray data show that the six oxygen atoms in the molecule are equivalently related to the tellurium atom. A representative salt is Ag_6TeO_6. Tin shows its expected co-ordination number of 6 in $CaSnO_3$. This crystallises with the perovskite structure, each tin being surrounded by six oxygen atoms at the corners of a regular octahedron, and each oxygen atom being common to two octahedra in such a way as to make the entire crystal one giant molecule of the formula $(CaSnO_3)_\infty$. Lastly, Pauling examines the case of the antimonates, and holds that they are satisfactorily formulated by assigning to antimonic acid the structure $H[Sb(OH)_6]$. That sodium antimonate can be written $NaSb(OH)_6$ had previously been suggested by L. P. Hammett.[6]

Important results have been obtained during recent years on the co-ordinated compounds of the alkali metals. N. V. Sidgwick and S. G. P. Plant[7] in 1925 published an account of the first recognised co-ordinated compounds of these metals when they described the lithium, sodium, and potassium derivatives of ψ-indoxyl*spirocyclo*pentane of the general formula $C_{12}H_{12}ON{\cdot}M{\cdot}C_{12}H_{13}ON$. All these compounds were decomposed immediately by water, regenerating the indoxyl compound. The sodium and potassium derivatives, however, could be crystallised from toluene although the lithium compound decomposed. Later, N. V. Sidgwick and F. M. Brewer[8] prepared further co-ordinated compounds of the alkali metals of which two typical examples are sodium *o*-nitrophenol salicylaldehyde (I) and lithium salicylaldehyde dihydrate (II). The latter, although a dihydrate, gives a colourless solution in toluene, thereby affording a clear proof that it is not an ionised but a covalent compound.

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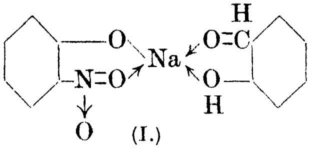
[4] C. A. Beevers and H. Lipson, *Z. Krist.*, 1932, **82**, 297; *A.*, 1932, 681.

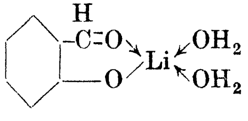
[5] L. Pauling, *J. Amer. Chem. Soc.*, 1929, **51**, 1010; *A.*, 1929, 748.

[6] See *ibid.*, 1933, **55**, 3052; *A.*, 919.

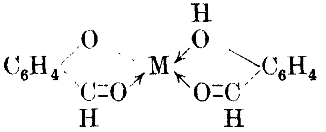
[7] *J.*, 1925, **127**, 209; *A.*, 1925, i, 298.

[8] *Ibid.*, p. 2379; *A.*, 1926, 71.


(I.)


(II.)

In 1931, H. King and G. V. Rutterford,[9] employing β-alanine, $NH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2H$, as the organic component, isolated derivatives of the type $LiX{\cdot}C_3H_7O_2N,1{\cdot}5H_2O$ (X = Cl, Br, or I), whilst in 1932 O. L. Brady and W. H. Bodger[10] recorded chemical evidence of chelation in the sodium salts of *o*-hydroxybenzaldehyde. More recently, O. L. Brady and M. D. Porter[11] have described some stable quadricovalent orange-coloured compounds of the alkali metals, prepared from reactions involving 4-*iso*nitroso-1-phenyl-3-methyl-5-pyrazolone. Particular value, however, attaches to the work of N. V. Sidgwick and F. M. Brewer[12] on the derivatives with salicylaldehyde, for all the alkali metals will co-ordinate with this unit to produce the simple structure (III).


$$\mathrm{C_6H_4}\begin{matrix}\mathrm{O}\\ \mathrm{C{=}O}\\ \mathrm{H}\end{matrix}\!\!\rightarrow\mathrm{M}\leftarrow\!\!\begin{matrix}\mathrm{H}\\ \mathrm{O}\\ \mathrm{O{=}C}\\ \mathrm{H}\end{matrix}\mathrm{C_6H_4}$$
(III.)

In certain cases a further molecule of the aldehyde can be co-ordinated. The experimental results have established the following covalency numbers for the alkali metals: lithium and sodium, 4; potassium, rubidium, and cæsium, 4 and 6. In this series, the 4-covalent compounds of sodium and potassium are much more stable than the others, whilst the potassium derivative with a covalency of six is formed only with difficulty. Sodium may, however, under appropriate conditions, also exhibit a covalency of six. The isolation of the compound NaQ,2HS (where HQ = $\frac{1}{2}$ quinizarin, and HS = salicylaldehyde) proves this.[13]

Considerable interest attaches to recent work on the co-ordination compounds of the currency metals. By the classical methods of stereochemistry, copper, like arsenic, has been shown to be tetrahedral when its co-ordination number is 4 and octahedral when it is 6. The resolution of the copper derivative of benzoylpyruvic acid by W. H. Mills and R. A. Gotts[14] in 1926 established that copper may have a tetrahedral structure in its 4-covalent compounds, whilst the resolution of the co-ordination compound $[Cu(en)_2 2H_2O]X_2$ by W. Wahl[15] in 1927 demonstrated the octahedral configuration of this 6-covalent compound. This latter resolution was achieved through the tartrate, and the active fractions could be converted into active iodides. N. V. Sidgwick[16] has recently emphasised the surprising nature of these experimental results. He points out that copper is generally unwilling to form 6-co-ordinated compounds and readily stops at 4. However, this complex ion must be remarkably stable, for if the water were even partly split off in solution the compound would racemise. He concludes that, although this stability is unexpected, there is no doubt that the attachment of chelate groups to an atom may either increase or diminish its power of further co-ordination.

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[9] *J.*, 1931, 3131; *A.*, 1932, 150.

[10] *J.*, 1932, 952; *A.*, 1932, 513.

[11] *J.*, 1933, 840.

[12] *J.*, 1925, **127**, 2379; *A.*, 1926, 71; *J.*, 1931, 361; *A.*, 1931, 443.

[13] N. V. Sidgwick and F. M. Brewer, *J.*, 1925, **127**, 2379; *A.*, 1926, 71.

The value of co-ordination in stabilising unstable simple salts is well known. This is particularly well illustrated by some recent results obtained by co-ordinating ethylenethiourea (etu; IV) with cuprous, argentous, and aurous salts. G. T. Morgan and F. H. Burstall[17] have shown that cuprous nitrate, which appears incapable of existence as a simple salt, forms the stable $[Cu\ 4etu]NO_3$, whilst unstable cuprous sulphate becomes quite stable as $[Cu\ 3etu]_2SO^4$. Moreover, the co-ordination compounds of silver chloride and silver bromide, [Ag 3etu]Cl and [Ag 2etu]Br, are not affected by light. Further, aurous chloride, which is readily decomposed by hot water to auric chloride and gold, gives the extremely stable $[Au\ 2etu]Cl,H_2O$. The co-ordination compound $[Au\ 2etu]NO_3$, where the central atom has an effective atomic number of only 82, is a very stable complex salt which crystallises unchanged from boiling solutions and is not reduced to metallic gold by formaldehyde.

It is generally stated that when copper is exposed to the atmosphere it becomes coated with a green basic carbonate. W. H. J. Vernon and L. Whitby[18] find, however, from analyses of typical patinas, that the older specimens are identical in composition with the mineral brochantite which may be formulated as (V). Near the coast, the sulphate ion may be replaced, in varying degree, by the chlorine ion, giving the analogue of the mineral atacamite. The preparation by O. L. Brady and E. D. Hughes[19] of co-ordination compounds such as (VI) involving 2 : 2′-diphenol as a chelate group adds interesting examples to the limited number of cases where a chelate ring may contain more than six atoms.

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[14] *J.*, 1926, 3121; *A.*, 1927, 149.

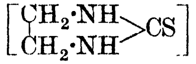
[15] *Acta Sci. Fennicae*, Comm. Phys. Math., 1927, **4**, 1; *A.*, 1928, 395.

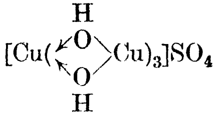
[16] "The Covalent Link in Chemistry," 1933, p. 202.

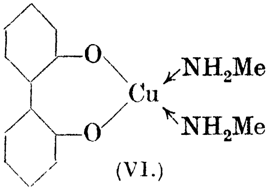
[17] *J.*, 1928, 143; *A.*, 1928, 278.

[18] *J. Inst. Metals*, 1930, **44**, 389; *B.*, 1930, 992.

[19] *J.*, 1933, 1227.

(IV.)

$$\left[\begin{array}{l}CH_2\cdot NH\\ CH_2\cdot NH\end{array}\!\!>CS\right]$$

(V.)

$$[Cu(\begin{array}{c}H\\ \swarrow O \searrow\\ \nwarrow O \nearrow\\ H\end{array}Cu)_3]SO_4$$



(VI.)

T. S. Moore and (Miss) M. W. Young [20] have directed their attention to the problem of the relative stability of copper derivatives of β-diketo-compounds. They find that the co-ordinating affinity decreases in the order (1) dibenzoylmethane, (2) acetylacetone, (3) benzoylacetone, (4) acetonedicarboxylic ester, (5) acetoacetic ester, and that there is a large gap between (3) and (4). This is almost the order representing the percentage of enol form in the pure substance [21] and affords strong confirmation of the view that the enol forms of β-diketo-compounds are chelated.[22]

Co-ordination with suitable units enables many metals to display valencies not shown in their stable simple salts. Silver is most interesting in this respect. It is stated that silver and fluorine may form an unstable black material which contains *ca.* 75% AgF_2.[23] Many stable co-ordination compounds of bivalent silver have, however, been isolated in recent years. As far back as 1912, G. A. Barbieri prepared the compound $[Ag\,4py]S_2O_8$ by mixing aqueous solutions of potassium persulphate and silver nitrate containing excess of pyridine. In 1927 he obtained the nitrate $[Ag\,4py](NO_3)_2$ by anodic oxidation of silver nitrate in the presence of pyridine, and in the following year W. Hieber and F. Mühlbauer, substituting *o*-phenanthroline (phenan) for pyridine, obtained a series of argentic salts of the general formula $[Ag\,2phenan]S_2O_8$ or X_2, where $X = HSO_4$, NO_3, ClO_3, or ClO_4. Later G. T. Morgan and F. H. Burstall stabilised the bivalent silver ion in a number of compounds by employing 2 : 2′-dipyridyl as a chelate group,[24] and recently G. A. Barbieri [25] has applied the electrolytic method to isolate similar compounds containing dipyridyl. He has also prepared a new type of complex compound of bivalent silver by using picolinic acid as the associating unit.[26] Silver picolinate, on oxidation with either potassium persulphate or anodic oxygen, gives an orange-red crystalline compound of the composition $Ag(C_5H_4NCO_2)_2$, which with hydrochloric acid gives silver chloride and chlorine. Presumably this is the internally complex compound (VII).

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[20] *J.*, 1932, 2694; *A.*, 1933, 36.

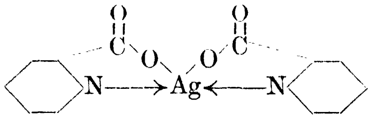
[21] K. H. Meyer, *Annalen*, 1911, **380**, 242.

[22] N. V. Sidgwick, "Electronic Theory of Valency," p. 147.

[23] M. S. Ebert, E. L. Rodowskas, and J. C. W. Frazer, *J. Amer. Chem. Soc.*, 1933, **55**, 3056; *A.*, 916.

[24] *Ann. Reports*, 1931, **28**, 132.

[25] *Atti R. Accad. Lincei*, 1932, [vi], **16**, 44; *A.*, 1933, 34.



(VII.)

The possibility that in some of these compounds the bivalency of the complex is not due to a bivalent silver ion but to incomplete co-ordination of the nitrogen atoms, leaving one of them free to function as a base, has been examined from the point of view of magnetic susceptibilities. In the univalent condition the ions of copper and silver possess a complete sub-group of 10 electrons and hence should be diamagnetic. On the other hand, the bivalent ions have only 9 electrons in this group and therefore should be paramagnetic. S. Sugden[27] has described the results he has obtained from measurements of the magnetic susceptibilities of 10 compounds of copper and 9 compounds of silver. From these, and other data in the literature, it is found that both copper and silver in the univalent condition have zero magnetic moments, whilst the bivalent atoms of these elements exhibit moments of 1·72—2·16 Bohr units. Amongst the compounds examined were the salts $[Ag\,4py]S_2O_8$, $[Ag\,2dipy]S_2O_8$, $[Ag\,3dipy](ClO_4)_2$. In every case these salts were paramagnetic, with moments of the same order of magnitude as those of bivalent copper. These results provide strong evidence for the view that the bivalency of the complex is due to the presence of a bivalent silver ion. W. Klemm[28] has also published data for the magnetic susceptibility of $[Ag\,4py]S_2O_8$ and $[Ag\,2(phenan)]S_2O_8$ which support this view. In 1907 J. Meyer and H. Eggeling[29] reported that colourless and yellow sodium silver thiosulphates existed. They were supposed to be isomerides, silver being attached to oxygen in the one case and to sulphur in the other. H. Bassett and J. T. Lemon[30] conclude from their experiments that this idea is erroneous, the colour difference being merely due to decomposition. They mention, however, that colourless and yellow sodium cuprous thiosulphates undoubtedly exist but that they are not isomeric.

Much fundamental work on the chemistry of tervalent gold has been done by C. S. Gibson and his collaborators. Tervalent gold is commonly 4-covalent, and this is substantiated by the observation of Gibson and J. L. Simonsen[31] that diethylgold bromide is bimolecular in benzene (VIII) and that with ethylenediamine or thallous acetylacetone it yields the complex salts (IX) and (X).

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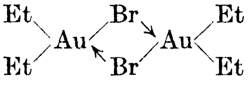
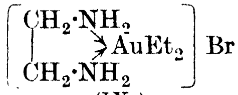
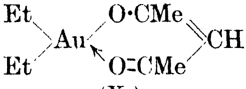
[26] *Atti R. Accad. Lincei*, 1933, [vi], **17**, 1078.

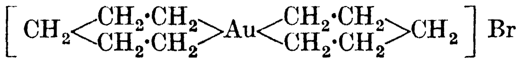
[27] *J.*, 1932, 161; *A.*, 1932, 324. [28] *Z. anorg. Chem.*, 1931, **201**, 32; *A.*, 1932, 10.

[29] *Ber.*, 1907, **40**, 1351; *A.*, 1907, ii, 347. [30] *J.*, 1933, 1424.

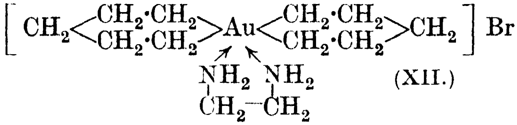
(VIII.) (IX.) (X.)

In 1931 Gibson and W. M. Colles[32] isolated the following interesting examples of 4-covalent gold, $[Au(en)_2]Br_3$, $[Au\ 2py\ Br_2]Br$, and $[Au\ py\ Br_3]$, and quite recently Gibson[33] has announced the preparation of two auric derivatives of unusual type, (XI) and (XII).



$$\left[CH_2{<}{\substack{CH_2\cdot CH_2\\ CH_2\cdot CH_2}}{>}Au{<}{\substack{CH_2\cdot CH_2\\ CH_2\cdot CH_2}}{>}CH_2 \right] Br$$

(XI.)



(XII.)

The second salt contains 6-covalent gold and is the first gold compound to be described in which the possibility of optical activity arises.

Another group of co-ordination compounds which has been investigated in recent years is that of thallium. Here, R. C. Menzies, N. V. Sidgwick, and their collaborators have made noteworthy contributions. It is remarkable that thallium forms no monoalkyl derivative. The trialkyl derivative, however, has been prepared by H. P. A. Groll in good yield from diethylthallium chloride and ethyl-lithium,[34] but one of the alkyl groups is very reactive, and the substance tends to form the stable dialkyl compounds which are salts of the strong base $Alk_2Tl\cdot OH$. It has been found that Et_2TlX can be conveniently prepared by the action of ethylmagnesium bromide on thallous chloride or thallous ethoxide.[35] Amongst the different investigations, one of particular interest is directed to determine whether the derivatives of the dimethyl and the diethyl base $Alk_2Tl\cdot OH$ with β-diketones, acetoacetic ester, and salicylaldehyde are chelate compounds or not.[36] The presence of the two alkyl groups would give the thallium in a monochelate derivative a stable covalency of four. The products, which are of the type Alk_2TlA (where A is a radical of the diketone or similar substance), prove to have unusual properties. They are crystalline solids which can be sublimed with ease under reduced pressure and are readily soluble in benzene, indicating that they are chelate compounds of the types (XIII) and (XIV). On the other hand, with

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[31] *J.*, 1930, 2531; *A.*, 1931, 78.

[32] *J.*, 1931, 2407; *A.*, 1931, 1316.

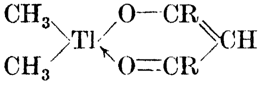
[33] *Nature*, 1933, **131**, 130; *A.*, 267.

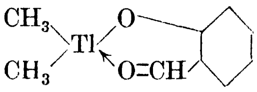
[34] *J. Amer. Chem. Soc.*, 1930, **52**, 2998; *A.*, 1930, 1302.

[35] R. C. Menzies and I. S. Cope, *J.*, 1932, 2862; *A.*, 1933, 152.

[36] R. C. Menzies, N. V. Sidgwick, E. F. Cutcliffe, and J. M. C. Fox, *J.*, 1928, 1288; *A.*, 1928, 745.

(XIII.)





(XIV.)

the exception of the benzoylacetone compounds, they are extremely soluble in water, yielding solutions with a strong alkaline reaction. Evidently, in water, these derivatives, like hydrogen chloride, pass from the covalent to the ionised state. The alkyloxides and aryloxides of thallium, such as $TlOC_2H_5$ and $TlOC_7H_7$, behave similarly.[37] In water they are salts, but they dissolve in benzene and are presumably covalent in that solvent and in the solid state. These substances, however, do not display thallium with a covalency of one, for molecular-weight determinations in benzene show that they exist as four-fold polymerides. The structure of this complex is not yet settled, although some ingenious speculations are made as to its configuration. The formation of the stable four-molecular complex shows that unicovalent thallium is very unstable, and this may be correlated with the fact that as yet no monoalkyl derivative of thallium has been isolated. On the other hand, the great stability of the dialkylthallium radical makes it unlikely that here the valency group of the thallium is completed by co-ordination. It is interesting to find, therefore, that an examination of the crystal structure of dimethylthallium iodide, $TlMe_2I$, has disclosed that the C–Tl–C atoms lie in a straight line.[38] This evidence suggests, according to N. V. Sidgwick,[39] that for 2-covalent compounds of atoms with "incomplete octets," the structure is rectilinear.

Dithionic acid is generally considered to have the constitution $HO_3S{\cdot}SO_3H$, the two sulphur atoms being directly linked. Confirmation of this view is afforded from the *X*-ray examination of potassium dithionate.[40] Each sulphur in the ion $[S_2O_6]''$ is surrounded, approximately tetrahedrally, by three oxygen atoms and one sulphur atom. This accords with the formulation (XV). An

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[37] N. V. Sidgwick and L. E. Sutton, *J.*, 1930, 1461; *A.*, 1930, 1052.

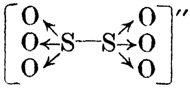
[38] H. M. Powell and (Miss) D. M. Crowfoot, *Nature*, 1932, **130**, 131; *A.*, 1932, 904.

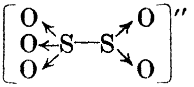
[39] *Op. cit.*, ref. (16).

[40] G. V. Helwig, *Z. Krist.*, 1932, **83**, 485; *A.*, 1933, 13.

X-ray examination of sodium metabisulphite, $Na_2S_2O_5$,[41] has disclosed that the structure of the S_2O_5 group is the same as that of the S_2O_6 unit, with one oxygen atom removed. Presumably it should be written as (XVI).

(XV.)





(XVI.)

T. M. Lowry and F. L. Gilbert[42] assumed the existence of single-electron links to the halogens in the co-ordination compounds α-Me_2TeX_2, where X = Cl, Br, or I, whereby an inert-gas structure is attained by the tellurium. These substances, however, proved to be diamagnetic, so they concluded that all the electrons were magnetically paired just as they are in compounds in which the valency electrons are present in pairs of shared electrons or as "lone pairs" of unshared electrons. If these compounds do contain single-electron bonds to the halogens there should be a paramagnetic effect due to the unpaired electrons. Actually, this will be masked by the diamagnetic effect of the rest of the molecule. However, if there is any paramagnetic effect it will be shown by the variation of magnetic susceptibility with temperature (since diamagnetism is independent of temperature). S. S. Bhatnagar and T. K. Lahiri[43] have examined the compounds α-Me_2TeR_2 (R = Br, I, NO_3) and find the susceptibility to be constant up to and beyond the melting point. Further, assuming all the bonds to be electron pairs, they have calculated the susceptibilities and find that they all agree with the observed values. They conclude therefore that there is no evidence for the single-electron bond in these substances.

The structure of the heteropoly-acids which are typical co-ordination compounds has long been a subject of speculation, and until recently chemists were content to adopt the Miolati–Rosenheim conceptions based on Werner's theory and to assign to the important 12-phosphomolybdic and -phosphotungstic acids the constitutions $H_7[P(R_2O_7)_6]$,aq., where R = Mo or W. In 1929, L. Pauling[44] on theoretical grounds gave the formula of the phosphotungstic acid as $H_3[PO_4W_{12}O_{18}(OH)_{36}]$. *X*-Ray investigations have now shown that the formula is best written as $H_3P(W_3O_{10})_4,nH_2O$ and that the other 12-heteropoly-acids have this structure.[45] The arrangement differs from that of Pauling. The complex acidic anion is a co-ordinated structure, more or less spherical. At the centre is one phosphorus, silicon, or boron atom, surrounding which are 4 oxygen atoms in the form of a tetrahedron. Each of these is common to three oxygen octahedra, making 12 octahedra in all. At the centre of each octahedron is a molybdenum or tungsten atom, *i.e.*, 12 altogether. In each group of three octahedra there is one common corner (one of the four central oxygen atoms) and three common edges, so that the whole complex has tetrahedral symmetry. The water of crystallisation packs in the interstices between the anions $[PW_{12}O_{40}]^{-3}$.

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[41] W. H. Zachariasen, *Physical Rev.*, 1932, **40**, 923; *A.*, 1932, 903.

[42] *Nature*, 1929, **123**, 85; *A.*, 1929, 127.

[43] *Z. Physik*, 1933, **84**, 671; *A.*, 1002.

[44] *J. Amer. Chem. Soc.*, 1929, **51**, 2868; *A.*, 1929, 1367.

[45] J. L. Hoard, *Z. Krist.*, 1933, **84**, 217; *A.*, 215; J. F. Keggin, *Nature*, 1933, **131**, 908; *A.*, 768.

Finally, some observations on the transition elements may be recorded. Here, covalencies of 8, 6, and 4 are possible. At present, little is known of the valency distribution with 8-covalent atoms, but without exception 6-covalent atoms have an octahedral arrangement. Amongst the transition elements, optically active 6-covalent compounds of iron, cobalt, rhodium, platinum, iridium, and ruthenium have been known for some time, and recently G. T. Morgan and F. H. Burstall,[46] by resolving trisdipyridylnickelous chloride, $[Ni\ 3dipy]Cl_2,6H_2O$, have added nickel to the list.

Molecular dissymmetry amongst purely inorganic compounds is very rare. Unusual interest attaches therefore to the preparation by F. G. Mann [47] of the optically active 6-covalent rhodium derivative $Na[(2H_2O)Rh(SO_2N_2H_2)_2]$.

In the 4-covalent compounds, the unique behaviour of certain of the transition elements is important. Whilst, in general, atoms with a covalency of 4 show a tetrahedral distribution of valencies, there are three exceptions to the rule, *viz.*, nickel, palladium, and platinum. As far back as 1893 Werner proposed a planar configuration in the case of platinum, and palladium was added later. Not until 1931, however, did L. Pauling,[48] from considerations based on wave mechanics, deduce that nickel, like palladium and platinum, should have a planar distribution of valencies in its 4-covalent compounds. Moreover, he asserted that the electronic formation of this plane configuration would involve a definite decrease of the (para) magnetic moment, so that in nickel it would become zero. The isolation by S. Sugden [49] of two isomeric forms of nickel benzylmethylglyoxime, coupled with the fact that, like the nickel derivatives of dimethyl- and diphenyl-glyoxime,[50] they are diamagnetic, is strong confirmation of Pauling's views. On the other hand, the chemical evidence for the plane structure of 4-covalent palladium compounds has proved to be valueless. Pink and yellow forms of the 4-covalent compounds $(NH_3)_2PdCl_2$, $(py)_2PdCl_2$, $(EtNH_2)_2PdCl_2$ have long been known, and in recent years, by analogy with the platinum derivatives, they have been considered as *cis*- and *trans*-isomerides of planar configuration. This view was supported in 1927 by the results of F. Krauss and F. Brodkorb,[51] who found that the compounds gave simple molecular weights in freezing phenol. In 1931, however, F. Krauss and K. Mählmann [52] repudiated these results, explaining that the nature of the solvent made them unreliable. They suggested instead that all the compounds were bimolecular. A re-examination of the substances by other investigators showed that, whilst the yellow forms had the simple formula, the pink were bimolecular and actually salts of the type $[Pd(NH_3)_4][PdCl_4]$.[53] This was proved by a variety of reactions and has been confirmed since by further work on the pallado-sulphines.[53a] Whilst, therefore, there is only one compound $(py)_2PdCl_2$, there is no doubt that there are two monomeric isomerides $(py)_2PtCl_2$,[54] and it is not unreasonable to suppose that these represent the *cis*- and *trans*-forms of a planar structure. Thus, in the case of platinum chemical evidence favours the planar configuration. Additional chemical evidence has been advanced by Tschernjaev in the isolation of three compounds

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[46] *J.*, 1931, 2213; *A.*, 1931, 1168. [47] *J.*, 1933, 412; *A.*, 580.

[48] *J. Amer. Chem. Soc.*, 1931, **53**, 1367; *A.*, 1931, 670.

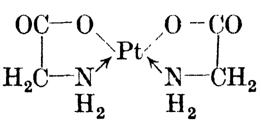
[49] *J.*, 1932, 246; *A.*, 1932, 272.

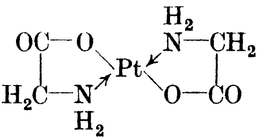
[50] W. Klemm, H. Jacobi, and W. Tilk, *Z. anorg. Chem.*, 1931, **201**, 1; *A.*, 1932, 10; L. Cambi and L. Szegö, *Ber.*, 1931, **64**, 2591; *A.*, 1932, 10.

$$[Pt(NH_3)(NH_2OH)(py)NO_2]_2[PtCl_4],$$[55]

and by A. A. Grünberg and B. W. Ptizyn,[56] who consider that they have prepared two compounds of the formulæ (XVII) and (XVIII).

(XVII.)





(XVIII.)

Lastly, H. D. K. Drew and F. S. H. Head [57] have found that by acting with *iso*butylenediamine upon β-$[(NH_3)(NH_2Et)PtCl_2]$ a mixture of two isomeric tetrammines results, which they have separated and characterised by their different plato-salts. Presumably these are the dichlorides of the planar structures (XIX) and (XX). A similar pair of isomeric β-platotetrammines $[Pt(NH_2{\cdot}CH_2{\cdot}CMe_2{\cdot}NH_2)_2]Cl_2$ has also been obtained in admixture and separated as two different plato-salts. All these examples seem to afford definite evidence of a planar structure for 4-covalent platinum.

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[51] *Z. anorg. Chem.*, 1927, **165**, 73; *A.*, 1927, 951.

[52] Siebert Festschr., 1931, 215; *A.*, 1932, 240.

[53] H. D. K. Drew, F. W. Pinkard, G. H. Preston, and W. Wardlaw, *J.*, 1932, 1895; *A.*, 1932, 824.

[53a] H. D. K. Drew, G. H. Preston, W. Wardlaw, and G. H. Wyatt, *J.*, 1933, 1294.

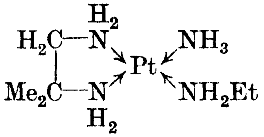
[54] A. Hantzsch, *Ber.*, 1926, **59**, 2761; *A.*, 1927, 93.

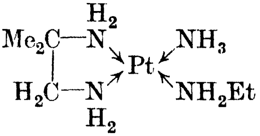
[55] *Ann. Inst. Platine*, 1928, **6**, 55; *A.*, 1928, 974.

[56] *J. pr. Chem.*, 1933, [ii], **136**, 143; *A.*, 381.

[57] *Nature*, 1933, **132**, 210; *A.*, 1040.

(XIX.)





(XX.)

Valuable information on this matter has been obtained during recent years from the X-ray examination of co-ordination compounds of palladium and platinum. It will be recalled that R. G. Dickinson [58] in 1922 examined potassium chloro-palladite and -platinite by X-ray methods, and concluded that the four chlorines in the complex anion lay in a plane with the palladium or platinum atom. In 1932 [59] E. G. Cox showed by an X-ray investigation of $[Pt(NH_3)_4]Cl_2,H_2O$ that the four nitrogen atoms lay in a plane with the platinum atom, whilst an examination of Magnus's salt $[Pt(NH_3)_4][PtCl_4]$ disclosed a similar distribution.[60] Quite recently, E. G. Cox and G. H. Preston [61] have carried out X-ray examinations of $[Pt(en)_2]Cl_2$, $[Pd(en)_2]Cl_2$, and $[Pd(NH_3)_4]Cl_2,H_2O$; all these compounds gave further evidence of the planar distribution of palladous and platinous valencies. In addition, the results have led to the conclusion that the valencies of the metal atom are not all crystallographically equivalent but are differentiated into pairs. More precisely, only those valencies which are *trans* to each other are equivalent. This applies to all the above compounds and also to $[Pt(NH_3)_4]Cl_2$. Whether this pairing is confined to the ammines is a matter for further investigation. They suggest that their work affords a physical basis for Werner's hypothesis of *trans*-elimination of groups from the tetrammines and triammines which has been proved to explain satisfactorily the reactions of a large number of mixed tetrammines and triammines, recently investigated.[62] Whilst it is certain from the X-ray results that the four covalencies are not crystallographically equivalent, it is possible that this may be explained as being due to polarisation forces in the crystal. However, if this were the explanation, it would be expected that the effect would be found in many other substances such as potassium chloroplatinite, particularly as the negative ion $[PtCl_4]''$ is more polarisable than the positive ion $Pt(NH_3)_4^{\cdot\cdot}$. Experimental evidence shows this is not the case.[61] It is interesting to find that the α-tetrachloride derived from the chlorination of α-$Pt(NH_3)_2Cl_2$ proves, on *X*-ray examination, to be suitably formulated with the ammonia groups in *trans*-positions in accordance with Werner's view of its configuration (XXI). Whilst the results for the β-tetrachloride were not so definite, they could be most simply explained by an octahedral distribution of valencies with the ammonia groups in *cis*-positions.

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[58] *J. Amer. Chem. Soc.*, 1922, **44**, 774, 2404.

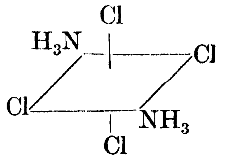
[59] *J.*, 1932, 1912; *A.*, 1932, 797.

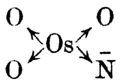
[60] E. G. Cox, F. W. Pinkard, W. Wardlaw, and G. H. Preston, *J.*, 1932, 2527; *A.*, 1933, 41.

[61] *J.*, 1933, 1089; *A.*, 1040.

[62] F. W. Pinkard, H. Saenger, and W. Wardlaw, *J.*, 1933, 1056; *A.*, 1001.

(XXI.)





(XXII.)

From time to time resolutions of 4-covalent nickel, palladium, and platinum compounds have been described,[63] but in no case has the investigator replaced the active radical used by an inactive one whilst still retaining the optical activity. It still remains, therefore, an interesting problem whether these three elements can give configurations other than planar when they are 4-covalent. In the case of the ββ'β''-triaminotriethylamino (tren) platinous salt [64] a planar configuration is unsatisfactory for the molecule. Here again the position is uncertain since it is not known whether the compound is unimolecular or not. An *X*-ray examination of $Ni(tren)SO_4$,[64] which is known to be monomeric, would be very useful. F. Rosenblatt and A. Schleede [65] have suggested that the resolutions published by H. Reihlen and W. Hühn [63] do not mean that the valencies of the platinum and palladium are non-planar. They consider that such results can be explained by asymmetry of the complex as a whole, the valencies remaining planar with the palladium and platinum atom. This may be true in the case of unsymmetrical chelate groups, but it seems most unlikely that the various unsymmetrical models proposed by them for compounds of the type $Pt(en)_2Cl_2$ have any real existence. The ion

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[63] H. Reihlen and W. Hühn, *Annalen*, 1931, **489**, 42; *A.*, 1931, 1167; 1932, **499**, 144; *A.*, 1933, 74; A. Rosenheim and L. Gerb, *Z. anorg. Chem.*, 1933, **210**, 289; *A.*, 497.

[64] F. G. Mann and (Sir) W. J. Pope, *J.*, 1926, 482; *A.*, 1926, 1233.

[65] *Annalen*, 1933, **505**, 51.

$Pt(en)_2^{\bullet\bullet}$ has in fact been shown to possess a symmetrical structure [61] different from any of those proposed by F. Rosenblatt and A. Schleede. These investigators [66] have recently questioned the existence of the third isomeride of $Pt(NH_3)_2Cl_2$ basing their conclusions entirely on the interpretation of their Debye diagrams. In view of the known difficulty of obtaining reproducible results by *X*-ray powder photographs of highly absorbing compounds of low symmetry, it is unfortunate that these authors give no details of their experimental technique. Their deduction from the published diagrams that this third isomeride is α- or *trans*-$Pt(NH_3)_2Cl_2$ whose lattice has been modified by the presence of a small quantity of β- or *cis*-$Pt(NH_3)_2Cl_2$ seems unjustified and opposed to all the chemical evidence. An interesting example of a 4-covalent atom is osmium in the osmiamates such as $K[OsO_3N]$. F. M. Jaeger and J. E. Zanstra [67] have recently shown that the ion $[OsO_3N]'$ is very nearly tetrahedral. The nitrogen is equivalent to the oxygen atoms as far as *X*-ray considerations are concerned. This suggests that the structure is (XXII) and that the nitrogen carries the negative charge. The per-rhenates $MeReO_4$ [68] have the same structure as the osmiamates.

In conclusion, it may be mentioned that much valuable information on co-ordination compounds will be found in " A Survey of Modern Inorganic Chemistry " by G. T. Morgan [69] and in his recent publication on " Experimental Researches on Co-ordination." [70] Also the new book by N. V. Sidgwick [71] on " Some Physical Properties of the Covalent Link " deals with many important aspects of co-ordination compounds.

The undersigned gratefully acknowledges the valuable help of Mr. E. G. Cox.

W. W.

5. THE COVALENCY RULE.

The covalency rule [1] is the generalisation that the maximum covalency of an element is limited in accordance with its period in the Periodic Table, being 2 for hydrogen, 4 for elements of the first short period (Li—F), 6 for those of the second short period

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[66] *Ber.*, 1933, **66**, [*B*], 472; *A.*, 476.

[67] *Proc. K. Akad. Wetensch. Amsterdam*, 1932, **35**, 610, 787; *A.*, 1933, 13.

[68] F. M. Jaeger and J. Beintema, *ibid.*, 1933, **36**, 528; *A.*, 892.

[69] Institute of Chemistry, 1933.

[70] Reprinted from the Acharyya Sir P. C. Rây Commemoration Volume, 1932.

[71] The George Fisher Baker Non-resident Lectureship in Chemistry at Cornell University, Cornell University Press, 1933.

[1] N. V. Sidgwick, " Electronic Theory of Valency," 1927, p. 152.

(Na—Cl) and the first long period (K—Br), and 8 for elements of higher atomic number. That in the first short period the limit is 4 was suggested by Werner, who pointed out that this might account for the chemical inactivity of carbon tetrachloride. The extension to the rest of the Periodic Table was made in practically its present form in 1923.[2] It is of interest to see how far the validity of the rule has been affected by the developments and discoveries of the last ten years.

In the nature of the case, the evidence in its favour is largely negative: that no compounds have been found which conflict with it. This test it has stood satisfactorily. Of the numerous compounds discovered in the last ten years, whose molecular weights have been determined, there is none in which an atom shows a higher covalency than the rule permits. A few compounds which appeared to contradict it have been shown not to exist, or to be compatible with it. For instance, a supposed 8-covalent cobalt compound was found by W. R. Bucknall and W. Wardlaw[3] to be really 6-covalent. Again, the highly complex borotungstates, which were written $R_9[B(W_2O_7)_6]$, were claimed as proving that boron could have a covalency of six, whereas the rule required that it should be limited to four. It has, however, recently been found[4] that in these compounds, as in the phosphotungstates,[5] the boron atom is surrounded by four oxygen atoms and is therefore 4-covalent, in the same way as the central beryllium atom in the " basic " beryllium acetate $Be_4O(CO{\cdot}CH_3)_6$.[6]

On certain points, however, direct evidence has appeared in favour of the rule. The first of these is from the side of theoretical physics. The theory of the covalent link elaborated by Heitler and London[7] seems to suggest that the maximum covalency of an atom is equal to one-half of the number of electrons in its outermost quantum group, so that the covalency maxima should be 4, 9, 16, whereas the chemical evidence indicates that they are 4, 6, 8. The theory of molecular orbitals developed by J. E. Lennard-Jones[8] and R. S. Mulliken[9] seems to be leading to a result more in accordance with the chemical evidence. Their methods have a more geometrical basis than those of Heitler and London. They consider the quantum groups and sub-groups of the molecule as a whole, and find that these are usually different from those of an atom isolated in space. The method suggests that in an octahedral group, for instance, there is an outer quantum sub-group which requires twelve electrons to fill it, and in a molecule of the type XY_6 six of these may be contributed by X and one each by the Y's. Detailed consideration of the electron structure of different molecular arrangements indicates that the tetrahedral arrangement will be succeeded by an octahedral, and that perhaps by a cubic, which would give the observed covalency values of 4, 6, 8.

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[2] N. V. Sidgwick, *Trans. Faraday Soc.*, 1923, **19**, 469; Sidgwick and R. K. Callow, *J.*, 1924, **125**, 532; *A.*, 1924, i, 506.

[3] *J.*, 1928, 2648; *A.*, 1928, 1345.

[4] J. F. Keggin, unpublished work.

[5] See this vol., p. 105.

[6] (Sir) W. H. Bragg and G. T. Morgan, *Proc. Roy. Soc.*, 1923, [*A*], **104**, 437; *A.*, 1924, i, 7.

[7] See C. N. Hinshelwood, *Ann. Reports*, 1930, **27**, 14—17.

[8] *Trans. Faraday Soc.*, 1929, **25**, 668; Faraday Soc. discussion, Sept. 1933.

[9] *Physical Rev.*, 1932, **40**, 55; **41**, 49, 751; 1933, **43**, 279.

Another point is the covalency maximum of 2 for hydrogen. On the chemical side there is no reason to doubt this. It is required to account for the association of hydroxylic compounds, the existence of the ion $[F_2H]'$, the peculiar non-associated character of *o*-nitro- and aldehydo-phenols and of the enolic forms of β-diketones, the action of water on the binary halides, etc. But on the physical side the position is not so simple. It was originally assumed that a covalency of 2 implied a group of 4 shared electrons. The physical objections to this are very strong. We know that an atom cannot have more than 2 electrons in the first quantum group, and if the hydrogen in these molecules has four, two of these must be in the second quantum group. But the energy with which 2-quantum electrons would be held is too small to account for the stability of the co-ordinated hydrogen. It seems more probable, therefore, that we have to deal with some kind of resonance between two structures, in the first of which the hydrogen is attached to one, and in the second to the other, of the two atoms which it holds together:

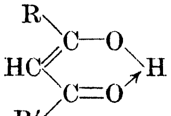
$$\mathrm{R : H \quad :R} \quad \rightleftharpoons \quad \mathrm{R: \quad H : R}$$

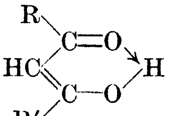
If such resonance is possible, it will involve a lower energy state than either of the two separate structures; that is, the resonance condition will be stable. The time of change from one structure to the other (if, indeed, we are allowed to speak of such a change) will be excessively short, and can involve an oscillation only of the electrons and not of the hydrogen nucleus, which is too heavy to oscillate with the necessary frequency.

Whatever may be the exact mechanism of the co-ordinated hydrogen, its occurrence is beyond doubt; we have good evidence that a hydrogen atom can hold two other atoms together, as in the examples quoted above. It has also recently been found possible to determine the dimensions of a hydrogen atom in this state, by means of *X*-ray measurements of crystal structure. These do not of course show the position of the hydrogen, but they give the distance between the nuclei of the two atoms which the hydrogen links. Thus W. H. Zachariasen[10] has shown that in sodium bicarbonate, $NaHCO_3$, there is a unique distance between one pair of oxygen atoms in two neighbouring CO_3 groups, and this can only be the pair which are united through the co-ordinated hydrogen O—H←O. This distance is 2·55 Å.U., the other distances between oxygens of neighbouring CO_3 groups being all close to 3·15 Å.U. Precisely the same distance (2·55) has been found[11] in potassium dihydrogen phosphate, KH_2PO_4. On the reasonable assumption (see below) that the hydrogen valencies lie in the same straight line, the distance between the oxygen nuclei in O—H←O is twice the radius of the oxygen plus the diameter of the co-ordinated hydrogen. The oxygen radius being 0·70 Å.U., we get 1·15 Å.U. as the diameter, or 0·58 Å.U. as the radius, of the co-ordinated hydrogen atom. Nearly the same result is obtained from the structure of the F—H←F ion in the " acid " fluorides;[10] the distance F · · · F is found to be 2·36 Å.U., and subtracting twice the radius (0·68) of the fluorine atom we get 0·50 as that of the hydrogen. These values are markedly larger than the radius of the ordinary 1-covalent hydrogen atom, which is 0·37 Å.U.; but the influence of the extra electrons will enlarge the radius; that of the negative hydrogen ion H' is 1·3, but this includes an " envelope " of perhaps 0·5, which would make the true radius of the ion 0·8 Å.U.

This conception of the co-ordinated hydrogen is in accordance with many of its properties. In its chelate compounds, such as those of the β-diketones (as well as in the metallic derivatives), it has long been evident that the unsymmetrical formulæ which are usually employed, *viz.*, (I) and (II), do not really represent the

(I.)





(II.)

facts: that it is not to be supposed that one of the oxygen atoms has permanently a different relation to the hydrogen (or the metal) from the other, and that if there is any difference between the two it must be supposed to oscillate from one form to the other like the double links in the Kekulé formula for benzene. This has been confirmed by the observation[12] that the electrical dipole moment of beryllium acetylacetone (1·18 D.) is not more than might be expected from the flexibility of the molecule, and far less than should result from the presence of two fixed co-ordinate links.

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[10] *J. Chem. Physics*, 1933, **1**, 634.

[11] J. West, *Z. Krist.*, 1930, **74**, 306; *A.*, 1931, 289.

[12] L. E. Sutton, *Proc. Roy. Soc.*, 1931, **133**, 668.

Such an alternation is in agreement with the theory that in the hydrogen compounds there is an oscillation between the two structures, and this would also explain the absence of isomeric enols in diketones (or keto-esters) in which R and R′ (above) are different.

It has been objected that the enols are unlikely to have chelate structures analogous to those of the metallic derivatives, because the great difference in size between a hydrogen atom and that of a metal will introduce too much strain into the ring. This objection can be shown to be of small weight. The atoms of the heavier elements are not so much larger than that of the hydrogen as one might expect, as Table I shows:

TABLE I.

Radii of neutral atoms (Å.U.).

—H←	Li	Be	Mg	Zn	Pt	Th	U
0·58	1·50	1·12	1·60	1·32	1·38	1·79	1·49

The strain due to the small size of the hydrogen is also relieved in another way. It has been shown [13] that when a 2-covalent atom has less than an octet of valency electrons, like thallium in $[Tl(CH_3)_2]^+$ or mercury in $Hg(C_6H_5)_2$, the natural angle is not 110° but 180°, and it is probable that this angle is more easily distorted from its natural value. Hence in a chelate 6-ring the effect on the strain of the small size of the hydrogen atom will be to some extent compensated by the larger angle between its valencies.

The recognition of the fact that the valency angle in co-ordinated hydrogen is 180° removes another difficulty, that of formulating the dimeric molecules of the carboxylic acids. Such acids, of course, readily polymerise in non-ionising solvents (some even in the vapour) up to double molecules, but no further. It should be possible to explain both why the polymerisation occurs, and why it stops at this point instead of proceeding indefinitely, as it does with the alcohols and phenols. It is clear that in (III) the hydrogen has a strong tendency to act as an acceptor, and the doubly linked oxygen as a donor. Co-ordination within the molecule to (IV) is impossible, because the strain in a 4-ring would be too great; if it occurred, acetic acid would behave as a non-associated substance, like salicylic aldehyde, where intramolecular co-ordination gives a stable 6-ring. In the acid, co-ordination must therefore take place between molecules, and if we suppose it to occur twice, we get the symmetrical dimeric structure (V). This would have no power of further co-ordination, which would explain why the

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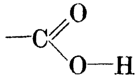
[13] See N. V. Sidgwick, "The Covalent Link," 1933, p. 230.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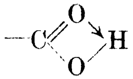
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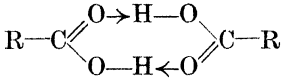
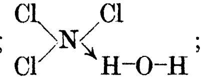

(V.)

association stops at this point; it should also have a low dipole moment, which is found to be the case.[14] The formula is also in agreement with the crystal structures.[15] The one objection that could be urged against it was that chelate rings of as many as 8 atoms are almost unknown.[16] Now that we realise that the covalencies of the hydrogen are in one straight line, it is evident that the symmetrical introduction of two hydrogen atoms into a 6-ring as in the formula above will not increase the strain.

Further evidence in favour of the covalency rule has been afforded by the behaviour of the recently discovered fluorides of nitrogen and oxygen NF_3 and OF_2. It has already been pointed out[17] that the behaviour of different binary halides with water can be explained if we assume that reaction takes place through a compound formed (not necessarily to more than a minute extent) by co-ordination between the central atom of the halide and the oxygen or the hydrogen of the water; and that this theory gives support to the covalency rule, and indicates where the covalency maximum changes. For example, in carbon tetrachloride the carbon, having already its maximum valency group fully shared, cannot co-ordinate and does not react, whilst in silicon tetrachloride, where the maximum group is not 8 but 12, co-ordination to $Cl_4Si \leftarrow OH_2$ occurs, and is followed by hydrolysis; in the same way the hexafluoride of selenium (maximum 12) does not react with water, while that of tellurium (maximum 16) does so. On this hypothesis the hydrolysis of nitrogen trichloride to hypochlorous acid and ammonia is due to co-ordination between the nitrogen and a hydrogen atom of the water giving  ; this is followed by the loss of HOCl, which involves the replacement of the chlorine on the nitrogen by hydrogen. Nitrogen fluoride, NF_3, was discovered by Ruff in 1928.[17a] If we apply this theory of hydrolysis to it, we can see that the first stage, the formation of the co-ordination compound, should occur as easily as with nitrogen chloride, but that the second stage, which here would be the elimination of hypofluorous acid, is impossible, because that acid does not exist. Hence if this theory gives the actual (and only) method by which such halides can be hydrolysed, nitrogen fluoride should not be acted on by water. This is found to be the fact; the gas is unaffected by water or alkalis even on heating; it is only when it is sparked with steam or hydrogen that decomposition occurs, with the formation of hydrogen fluoride and the oxides of nitrogen. Oxygen fluoride OF_2 [18] is also remarkably inert, though less so than the nitrogen compound; it reacts with strong alkalis and acids, but is indifferent to water.[19] It is also remarkable that if the gas, at a low pressure or mixed with an inert gas, is treated with yellow phosphorus, the latter removes the oxygen from it, but has no action on the oxygen fluoride.[20] Dennis and Rochow have found that with concentrated alkali it gives an oxy-acid of fluorine, but have obtained evidence that this is not hypofluorous acid but fluoric acid, HFO_3.

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[14] C. P. Smyth and H. E. Rogers, *J. Amer. Chem. Soc.*, 1930, **52**, 1824; *A.*, 1930, 841.

[15] A. Müller, *J.*, 1923, **123**, 2043; A. Müller and G. Shearer, *ibid.*, p. 3156.

[16] See "Electronic Theory of Valency," p. 252.

[17] Sidgwick, *J.*, 1924, **125**, 2672; "Electronic Theory of Valency," p. 156.

[17a] O. Ruff, J. Fischer, and F. Luft, *Z. anorg. Chem.*, 1928, **172**, 417; *Z. angew. Chem.*, 1928, **41**, 1289; *A.*, 1928, 854.

Thus the behaviour of these fluorides supports the view that the reaction of halides with water takes place through an intermediate co-ordination compound; and if this view is accepted, the nature of the reaction with different halides is direct evidence of the truth of the covalency rule.

The Covalency Rule and Atomic Dimensions.

Some writers have argued that the increase of the covalency maxima with atomic number is merely a result of the sizes of the atoms, and that the reason why, for example, $[SiF_6]''$ can exist but not $[CF_6]''$ is only that there is not room for six fluorine atoms round the smaller carbon. It is interesting to consider this argument in detail, and see how it has been affected by the increase of our knowledge of atomic dimensions. It was first used by those who assumed that the general type of linkage was ionic, and that carbon tetrachloride, for example, should be written $C^{4+}(Cl^-)_4$. Now, in this question of the space available for attached atoms, it is of fundamental importance whether we regard the links as ionised or covalent, because the presence of a positive charge diminishes and that of a negative charge increases the atomic radius. This can be seen from Table II, which includes certain ions, such as C^{4+} and S^{6+}, whose radii can be calculated but cannot be observed, since they do not really exist, the molecules which were supposed to contain them being actually covalent.

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[18] P. Lebeau and A. Damiens, *Compt. rend.*, 1927, **185**, 652; *A.*, 1927, 1044; 1929, **188**, 1253; *A.*, 1929, 779; Ruff and W. Menzel, *Z. anorg. Chem.*, 1930, **190**, 257; *A.*, 1930, 877; Ruff and K. Clusius, *ibid.*, p. 267; *A.*, 1930, 986; H. von Wartenberg and G. Klinkott, *ibid.*, **193**, 409; *A.*, 1931, 42.

[19] The small solubility of these gases in water is no objection to the theory, since we need not suppose that more than a small concentration of the co-ordination compound is attained.

[20] L. M. Dennis and E. G. Rochow, *J. Amer. Chem. Soc.*, 1932, **54**, 832; *A.*, 1932, 485; 1933, **55**, 2431; *A.*, 797.

TABLE II.

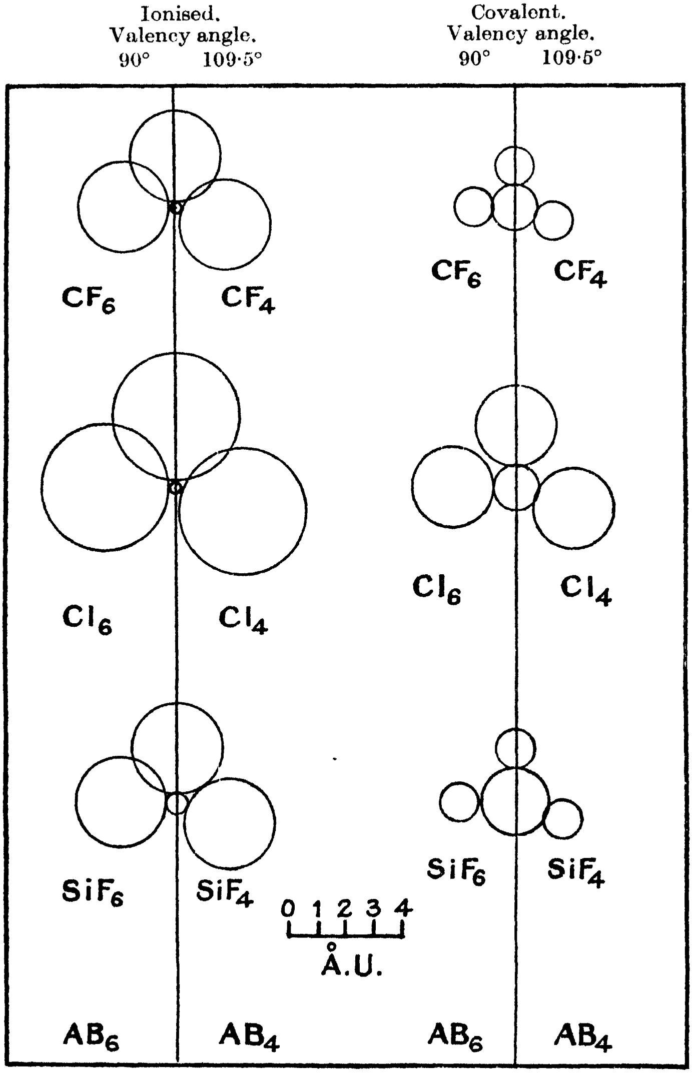
Radii of atoms and ions (Å.U.).

C	0·77	C^{4+}	0·2	Cl	0·97	Cl^-	1·81
Si	1·17	Si^{4+}	0·4	Br	1·13	Br^-	1·96
S	1·06	S^{6+}	0·32	I	1·35	I^-	2·19
F	0·68	F^-	1·33				

The geometry of the systems is simple. For AB_4 we have normally a tetrahedron, with a valency angle of 109·5°; for AB_6 the arrangement is octahedral, and the angle 90°; the same angle of 90° occurs in the rare cases where we have four covalencies in a plane, as with nickel; for a molecule AB_8 the structure is presumably cubic. We assume that the atoms are spherical, and that the condition of stability is that every B should be able to touch A. If a, b, are the radii of A and B, then the maximum values of b which permit of this are:

For AB_4 (tetrahedral) ... ... $b = 4{\cdot}45\,a$
For AB_6 (tetrahedral) or AB_4 (plane) ... $b = 2{\cdot}42\,a$
For AB_8 (cubic) ... ... $b = 1{\cdot}37\,a$

It is at once evident from these results and the radii in Table II that on the hypothesis of ionisation there is not room for the atoms of even so stable a molecule as carbon tetrafluoride; C^{4+} has a radius of 0·2 Å.U., and so the largest atom of which it could accommodate four would have a radius of 0·89, whereas even the fluorine ion is 50% larger than this (1·33 Å.U.). The results are shown graphically for carbon fluoride and iodide and for silicon fluoride, in the figure. In the left-hand series of diagrams the radii used are those of the ions (C^{4+}, Si^{4+}, F^-, I^-), and in the right-hand series those of the neutral atoms. Each of the six figures gives the positions of the atoms of the molecules AB_6 and AB_4; the halogen atom at the top makes a valency angle of 90° with that on the left of the central line, and one of 109·5° with that on the right. The B atoms are drawn to touch A, so that the condition of stability is that they should not overlap. When we pass from the ionised to the covalent figures the position is entirely changed, since the absence of charge makes A much larger and B smaller. It now appears that there is ample room, not only for the number of attached atoms in actual stable molecules, but for far more than are ever found; even in the imaginary CI_6 there would be space left between the iodine atoms; so that it would seem that the steric influence can have nothing to do with the covalency limits.



This is shown more fully in Table III, in which the ratio *b*/*a* (calculated for covalent links) is given for a series of atoms; as we have seen, the number of B's which can surround one A is 8, 6, or 4 if this ratio does not exceed 1·37, 2·42, and 4·45 respectively.

TABLE III.

Values of b/a *for covalent links.*

A =	C	O	Si	S
B = H	0·48	0·53	0·32	0·35
C	1·00	1·10	0·66	0·73
O	0·91	1·00	0·59	0·66
F	0·88	0·97	0·58	0·64
Cl	1·26	1·39	0·83	0·92
Br	1·47	1·61	0·97	1·07
I	1·75	1·93	1·15	1·27

On this basis there is room round an atom of carbon (whose observed covalency maximum is 4) for 8 atoms of fluorine or oxygen, and for 6 atoms of almost any kind, and round silicon or sulphur (where the maximum is 6) for eight atoms even of iodine.

The story does not, however, end here. It is certain that for these compounds the covalent picture is the true one, and this is now generally recognised. But it has become evident that this type of model, in which the atoms are represented by spheres, with radii calculated from the lengths of the links, is imperfect. Such models express satisfactorily the distances between the centres of linked atoms; but the distances between those of unlinked atoms, even when they belong to the same molecule, are much greater. We ought to regard the spheres as covered on their outsides with a sort of " envelope " which is of the order of 0·5 Å.U. in thickness; or to speak more scientifically, we have to take into account the mutual repulsion of the electrons of unlinked atoms, which is considerable even when the spheres of the simple model are 1 Å.U. apart.[21] The simplest example is afforded by carbon tetrachloride, in which the spheres representing the chlorine atoms are 1·05 Å.U. apart, or the " envelope " is 0·53 Å.U. thick, and yet the electronic repulsion is still strong enough at this distance to stretch the link by 0·09 Å.U., and to diminish the heat of its formation by some 3,500 calories. The magnitude of this repulsion, and its variation with the distance and with the nature of the atoms, cannot yet be calculated, but the example of carbon tetrachloride is enough to show that it seriously interferes with the usefulness of the simple spherical models, and that steric influences may play an important part in limiting the stability of molecules even where these models give no indication of their presence. At the same time it is doubtful whether size is the determining factor in fixing the covalency maxima. This can be seen if we calculate the thickness of the " envelopes " in a series of actual molecules, and compare them with those which would occur in molecules in which the covalency maxima were exceeded. The results for molecules of the type of CB_4 and SB_6, together with those for the imaginary type CB_6, are given in Table IV, being calculated on the values obtained for the atomic radii in unstrained links; the behaviour of carbon tetrachloride shows that in many of these molecules the links would be more or less stretched, and the "envelopes" correspondingly increased. It will be seen that the "envelope" would be practically the same in CF_6 as it is in CI_4.

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[21] See *Ann. Reports*, 1932, **29**, 67.

TABLE IV.

Thickness of "envelopes" (Å.U.).

	CB_4	(CB_6)	SB_6
B = F	0·51	0·35	0·55
Cl	0·45	0·26	0·46
Br	0·42	0·22	0·42
I	0·38	0·15	0·35
O	0·50	0·34	0·54

Whatever may be the true connexion between atomic dimensions and the covalency maxima, the evidence available up to date is entirely in favour of the covalency rule as expressing the relation of the values of these maxima to the position of the elements in the Periodic Table. N. V. S.

6. THE "INERT PAIR" OF VALENCY ELECTRONS.

This name has been given to the property observed in certain elements, especially in the heavier elements of the B sub-groups of the Periodic Table, of behaving in some compounds as if two of the valency electrons were absent, or had become part of the core. This results in the element resembling in these compounds the one which is two places in front of it: thus we have $Tl^{\cdot}$ like $Au^{\cdot}$, $Pb^{\cdot\cdot}$ like $Hg^{\cdot\cdot}$, ICl_3 and IF_5 like $SbCl_3$ and $SbCl_5$.

The theoretical reason for this has been pointed out by H. G. Grimm and A. Sommerfeld.[1] The maximum sizes of the quantum groups are given by $2n^2$, where n is the principal quantum number; they are 2, 8, 18, and 32. Now a group of 8, which is the maximum for the quantum number 2, can also behave as practically complete, showing no tendency to take in more electrons, even when its quantum number is 3, 4, 5, or 6, as we see in the outermost group in argon, krypton, xenon, and emanation; and in the same way 18 can act as a complete group in xenon and emanation, where its quantum number is 4 and 5 respectively. It is not clear why the same is not true of the group of 2, but in general it is not, and a closed group of 2 electrons is only found where its principal quantum number is 1. These instances of the inertness of the first two valency electrons of a group obviously occur in atoms in which this group of 2 is able to show something of the completeness which it has in helium or lithium.

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[1] *Z. Physik*, 1926, **36**, 36; *A.*, 1926, 560.

But while we can thus see how the phenomenon arises, we have no theoretical guidance as to where it will occur; we cannot give a reason even for its most obvious characteristic, that it is found chiefly among the heavier elements of the B sub-groups. Hence in order to discover the range of its occurrence we have to rely entirely on the chemical evidence, and examine the properties of the successive periodic groups in turn.

The inert pair manifests itself mainly in two ways: (1) in the monatomic cations and (2) in the covalent compounds. The outer electronic group of a cation is normally either a complete group of 8 or 18 electrons, or one of an intermediate size between these two, as in the transitional elements (in $Fe^{\cdot\cdot}$ 14, in $Fe^{\cdot\cdot\cdot}$ 13); a group of less than 8 electrons is too unstable to exist in an ion. Where, however, two of the electrons can become inert, we can have a stable ion with this pair as its outer group, as in $Sn^{\cdot\cdot}$ (2, 8, 18, 18, 2) or $Tl^{\cdot}$ (2, 8, 18, 32, 18, 2). In the covalent compounds the presence of the inert pair is shown in a different way. In general, a " mixed " valency group—one containing both shared and unshared electrons—is never larger than 8, though pure (wholly shared) groups of up to 16 electrons are, of course, well known. The only exceptions are when the atom contains an inert pair, and then it is always found that the valency group can be reduced to a normal form—either an octet or a wholly shared group—by the removal of two unshared electrons from the valency group to the core. For example in $SbCl_3$ and SbF_5 we have normal valency groups, in the former $2, \underline{6}$, a mixed octet, and in the latter $\underline{10}$, a fully shared decet (the shared electrons are underlined). In ICl_3 the iodine has the group $4, \underline{6}$, and in IF_5 $2, \underline{10}$; these are abnormal, but reduce to the normal forms of the antimony halides if two unshared electrons are considered as part of the core.

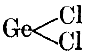
Thus the effect of the inertness of the pair is always to change the valency by two, but while it diminishes it in the ion, it increases it in the covalent compounds.

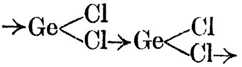
It need scarcely be said that no element exhibits the inert pair in all its compounds; there is always a number in which the pair is active; the strength of the tendency for it to assume the inert state varies greatly in different elements.

We may now consider the periodic groups in turn. There is no sign of the inertness in the A sub-groups, so that we are concerned only with the typical elements and those of the B sub-groups. The phenomenon obviously cannot occur in Group I. In Group II it would involve the disappearance of all the valency electrons, and the acquisition of a character like that of an inert gas. There are distinct signs of this in mercury; it is the only element other than the inert gases which gives a monatomic vapour in measurable concentration anywhere near the ordinary temperature. Cadmium and zinc show no such behaviour (b. p.'s Zn 906°, Cd 778°, Hg 357°). We may therefore recognise the inert pair as occurring to some extent in mercury, but in no other element of the second group.

Group III. The inert pair appears first in indium, which forms a unimolecular monochloride, InCl, which in the fused state is a good conductor of electricity, and must be supposed to contain $\mathrm{In}^{\bullet}$ ions; this chloride is very unstable and is decomposed by water. Gallium does not form a monochloride. The bivalent state of both gallium and indium is without parallel elsewhere in the Periodic Table, and is unexplained. In the covalent state, as we have seen, these lower valencies imply, not more than an octet, but less.

In thallium, as we should expect, the inertness is much more marked. The thallous ion $\mathrm{Tl}^{\bullet}$, with an outer group of two (inert) electrons, is quite stable, and resembles the ion of an alkali metal or silver. In the covalent thallous compounds, such as the alkoxides Tl·O·Alk, the imperfect valency group of two shared electrons tends to make itself up to 8 by polymerisation; the alkoxides form quadruple polymerides in which the octet is completed by co-ordination.[2]

Group IV. The evidence in this group needs to be examined with care. The bivalent state in general is very stable in lead, and the stability falls off steadily as we ascend the series until it is nearly zero in silicon; it then reappears in carbon. This, however, is no evidence of the inert pair where the compounds in question are covalent, as they are with carbon, silicon, and germanium; their simple formulation as $\mathrm{C}=\mathrm{O}$,  $\mathrm{Ge}{<}^{\mathrm{Cl}}_{\mathrm{Cl}}$ would give the atom a valency sextet. This will have a strong tendency to grow to an octet, which it can do by co-ordination. With carbon, as has been shown,[3] the co-ordination occurs within the molecule, as in $\mathrm{C}\overset{\leftarrow}{=}\mathrm{O}$. With silicon and germanium this is for some reason impossible, but the fact that the bivalent compounds of these elements are all solids shows that co-ordination takes place between molecules, as in



$$\rightarrow\mathrm{Ge}{<}^{\mathrm{Cl}}_{\mathrm{Cl}\rightarrow}\mathrm{Ge}{<}^{\mathrm{Cl}}_{\mathrm{Cl}\rightarrow}$$

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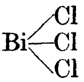
[2] Sidgwick and Sutton, *J.*, 1930, 1461.

[3] I. Langmuir, *J. Amer. Chem. Soc.*, 1919, **41,** 1543; D. Ll. Hammick, R. G. A. New, N. V. Sidgwick, and L. E. Sutton, *J.*, 1930, 1876; *A.*, 1930, 1239; Sidgwick, *Chem. Reviews*, 1931, **9**, 77.

with the completion of the octet and the production of a solid polymeric form. Why there should be this difference we do not know; it is perhaps due to a greater strain in the multiple links of silicon and germanium; the contrast between the volatile carbon monoxide and the non-volatile SiO and GeO obviously recalls that between carbon dioxide and silica. It is at any rate evident that we cannot infer the presence of the inert pair from the bivalent compounds of these elements when they are covalent, but only when they are ionised. The first element of the group to give bivalent ions is tin (there is no satisfactory evidence of a germanous ion). In lead, as usual, the inertness is much more marked; while the stannous ion is unstable, and readily passes into the stannic, with the reappearance of the activity of the pair, the plumbous ion $Pb^{\cdot\cdot}$ is the stable form, and has no reducing properties.

Group V. Hitherto our evidence of the inertness has been derived exclusively from the ions. In this group we have also a second line of argument, from the covalent compounds. The two may be taken separately. A tervalent cation of a fifth-group element has two of the electrons of its valency group left, obviously in an inert state. It has the structure: (core), 2, as have $Sn^{\cdot\cdot}$ and $Tl^{\cdot}$. Such an ion is not formed by nitrogen or phosphorus, and there is no good evidence of its occurrence with arsenic; but there are clear indications of the existence of an antimony ion $Sb^{\cdot\cdot\cdot}$, and with bismuth the phenomenon is very marked. There is a whole series of salts in which bismuth acts like a metal of the third group such as lanthanum, as in the isomorphous series of complex nitrates $M_3''[M'''(NO_3)_6]_2,24H_2O$, where M'' may be Mg, Zn, Co'', Ni; and M''' may be Bi, La, Ce, Pr, and other rare-earth metals. Thus the ionic evidence indicates that the inert pair begins with antimony.

When the tervalent ion passes into the covalent state, we merely have a normal octet produced, and the inactivity disappears; thus in $[Bi]Cl_3$ the bismuth has the structure (60)(18)2, and in  it has (60)(18) 2, $\underline{6}$; there is no doubt that the trihalides of antimony and bismuth are largely in the covalent state. But if a covalent derivative of this type forms a complex anion, this must contain an inert pair of electrons, because its valency group has increased beyond 8. For example, in $K[SbCl_4]$ the antimony, with five electrons to start with, has gained four more from the chlorines and one from the potassium: it has a decet with 8 shared electrons, 2, $\underline{8}$. In $K_4[BiI_7]$ the bismuth has the valency group 2, $\underline{14}$. As has been said, a mixed valency group with as many as 8 shared electrons is never found to have more than two unshared electrons, and this only when these two are inert.* Now there are a number of complex salts of this type derived from the trihalides of antimony and bismuth. In addition to those mentioned above we have $K[SbF_4]$, $K[BiCl_4]$, and $K_3[Bi(CNS)_6]$. No such complex derivatives of tervalent nitrogen or phosphorus have been described, nor until recently of tervalent arsenic. This year, however, W. Petzold[4] has described a series of salts of the types $M[AsCl_4]$, $M[AsBr_4]$, $M_2[AsCl_5]$, in addition to more complicated forms containing several atoms of arsenic in the molecule. The cations are alkylammoniums and pyridinium. The salts (the chlorides are colourless and the bromides pale brown or yellow) are soluble in concentrated halogen acids, but are at once decomposed by water. This is the only evidence we have of the occurrence of the inert pair in arsenic, and from the properties of the compounds it is clear that this state of the arsenic atom is very unstable.

It should perhaps be pointed out that the formation of complex anions from the pentahalides is no proof of the inert pair; $K[SbCl_6]$, for example, has a valency group of 12 shared electrons.

Group VI. This group raises questions of considerable interest. There is no doubt about the occurrence of the inertness in tellurium, which gives a definite quadrivalent cation $Te^{\cdot\cdot\cdot\cdot}$, with the structure 2, 8, 18, 18, 2. The evidence for a corresponding selenium ion $Se^{\cdot\cdot\cdot\cdot}$ is very weak.

Apart from the ions, we should look for evidence of the inertness in the tetrahalides such as XCl_4, with a valency group of (2) $\underline{8}$. Tellurium tetrachloride, though its melting point (214°) and boiling point (414°) are high, and the liquid from its high conductivity (0·1145 at 236°),[5] must be largely ionised, can evidently exist in the covalent state, since its vapour density at 536° is 90% of the theoretical value.

Selenium tetrachloride is a stable solid, but is relatively non-volatile, and its vapour density at 200° is only about half of that calculated for $SeCl_4$, indicating that it is largely dissociated into Se_2Cl_2 and chlorine. Selenium tetrafluoride, however,[6] melts at −13° and boils at 93° and is no doubt a genuine covalent compound.

The presence of the inert pair in tellurium and selenium is confirmed by the existence of complex salts derived from the tetrahalides, such as $K[TeCl_5]$, $K_2[SeBr_6]$, and $K_2[TeCl_6]$. Selenium tetrachloride is remarkable for forming a 1 : 1 addition compound with antimony pentachloride. This must have the structure $Cl_4Se{\rightarrow}SbCl_5$, the inertness having disappeared, and the selenium having acquired a valency group of 10 and the antimony of 12 shared electrons.

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[4] *Z. anorg. Chem.*, 1933, **214**, 355; *A.*, 1258.

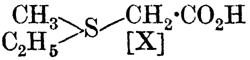
[5] A. Voigt and W. Biltz, *ibid.*, 1924, **133**, 297; *A.*, 1924, ii, 552.

[6] E. B. R. Prideaux, *J.*, 1928, 1603.

* The only exception to this rule is the series of salts of the type of $K[ICl_4]$, in which the iodine appears to have the valency group 4, $\underline{8}$, which on the assumption of the inert pair reduces to (2), 2, $\underline{8}$. As this stands as an isolated exception we may suppose that the true formula is a multiple of that given above; the molecular weight has not been determined.

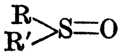
We may therefore conclude that the pair can be inert in tellurium and selenium.

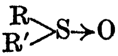
When we come to sulphur we find a different state of affairs. Sulphur tetrachloride, SCl_4, can only exist in the solid state at very low temperatures; it already has a dissociation pressure (giving SCl_2 and chlorine) of more than an atmosphere at $-30°$. Lowry [7] has shown that there is no reason to think that it exists at all in the liquid state in a solution of sulphur in chlorine. He has also pointed out that the dielectric constant of the solid tetrachloride is much higher than we should expect for anything but a salt, and he suggests not improbably that this substance, which can only exist as a solid and is apparently insoluble in a non-ionising solvent like liquid chlorine, is actually a salt, trichlorosulphonium chloride $[SCl_3]Cl$, in which, of course, the sulphur would have the normal octet structure 2, $\underline{6}$.

In the same way the active sulphonium compound of W. J. Pope and S. J. Peachey [8]  $\genfrac{}{}{0pt}{}{CH_3}{C_2H_5}{>}S{\genfrac{}{}{0pt}{}{\diagup CH_2{\cdot}CO_2H}{[X]}}$ has all the characteristics of a salt. It is non-volatile, it has a high melting point (if any), and it is precipitated from alcoholic solution by ether in a non-solvated form. The salt character of the sulphonium compounds is most clearly shown by comparing trimethylsulphonium iodide with tetramethylammonium iodide on the one hand and trimethyltin iodide—a genuine covalent compound—on the other :

$(CH_3)_4NI$.	$(CH_3)_3SI$.	$(CH_3)_3SnI$.
Decomposes without melting at 230°	Dissociates without melting at 214°	B. p. 170°
Sol. in water	Sol. in water	Sol. in water
Insol. in ether	Insol. in ether	Sol. in ether, benzene, etc.

Another strong indication that the sulphur atom cannot assume the true 4-covalent form, *i.e.*, that the pair cannot become inert, is derived from the optically active 3-covalent sulphur compounds, such as the sulphoxides. These might have two formulæ :


$\genfrac{}{}{0pt}{}{R}{R'}{>}S{=}O$


$\genfrac{}{}{0pt}{}{R}{R'}{>}S{\rightarrow}O$

Valency group, 2, $\underline{8}$. Valency group, 2, $\underline{6}$.

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[7] T. M. Lowry, L. P. McHatton, and G. G. Jones, *J.*, 1927, 746; T. M. Lowry and G. Jessop, *J.*, 1929, 1421; 1930, 782.

[8] *J.*, 1900, 77, 1072.

The first of these involves an inert pair, but the second does not; the activity of the compounds definitely rules out the first formula and establishes the second. Now, if the first structure could exist at all, it should be present in solution at least in small quantity in tautomeric equilibrium with the second; but every time an active molecule went over into it, it would lose its activity, and so the compound would racemise rapidly. The fact that the active sulphoxide does not racemise shows that the doubly linked form is not even temporarily assumed, and this implies that there is some fundamental objection to it, and the only one that can be suggested is that the inert pair which it involves cannot occur in sulphur.

One compound has been described which if it is real proves the possibility of the inert pair in sulphur. This is sulphur tetrafluoride SF_4. According to J. Fischer and W. Jaenckner,[9] this is formed by heating cobaltic fluoride, CoF_3, with sulphur, and is a colourless gas, m. p. $-124°$, b. p. $-40°$, mol. wt. 107 (theory 108), which when dry does not attack glass, sulphur, or rubber, but does attack mercury. If this exists it is obviously a covalent fluoride, and the sulphur atom has the inert pair. The evidence against the phenomenon in sulphur is so strong that an isolated exception needs careful scrutiny. The paper of Fischer and Jaenckner is called a "preliminary communication," and they have published no subsequent paper on the subject during the last four years, nor does Ruff, in his numerous papers on the fluorides, seem to have made any reference to it. Also the differences between the properties of the substance and those of the undoubted selenium tetrafluoride are far greater than we should expect the replacement of selenium by sulphur to produce, as may be seen by comparing the melting and boiling points of these compounds with those of the hexafluorides :

SF_4:	m. p. $-124°$,	b. p. $-40°$.	SF_6:	m. p. $-56°$,	b. p. $-62°$.
SeF_4:	,, $-13°$,	,, $+93°$.	SeF_6:	,, $-35°$,	,, $-39°$.

We may therefore assume provisionally that there is some mistake about sulphur tetrafluoride, and that the inert pair, which is very marked in tellurium and selenium, cannot appear in sulphur.

Group VII. In this group the evidence depends wholly on the covalent compounds; a simple cation with two inert electrons would have 5 positive charges, and this is more than any atom can carry. The covalent compounds of polyvalent halogens are of two types, neutral molecules, as ICl_3, and anions, as $[ICl_2]'$. In the anions of this type the linking atom has a valency group of 10, *i.e.*, 6, $\underline{4}$, which involves the inert pair, giving (2), 4, $\underline{4}$. It is well known that the trihalides are more stable the heavier their component atoms, and that the stability depends on the presence of one heavy atom in the complex; for example, while $[Cl_3]$ is almost if not quite unknown, $[ICl_2]$ is nearly as stable as $[I_3]$. This is what we should expect; in a trihalogen ion $\mathrm{A}<^{\mathrm{B}}_{\mathrm{B}}$ it is only the A atom which exhibits the inertness, and this is always more marked in the heavier atoms. Definite evidence that the heavier atom is in the middle of the complex is afforded by the crystal structure of $Cs[ICl_2]$.[10]

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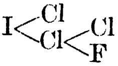
[9] *Z. angew. Chem.*, 1929, **42**, 810; *A.*, 1929, 1155.

For some reason, while iodine, bromine, and chlorine are almost equally ready to act as the terminal members of the complex ion, fluorine as a rule does not do so. This, of course, has no relation to the question of inertness; it is presumably due to the strong tendency of fluorine to pass from the covalent to the ionised state. Until lately it was not known that fluorine could ever form part of a polyhalide ion, although it forms neutral compounds with other halogens at least as easily as any other element of the group. Recently Booth and his co-workers [11] have prepared the salts $Cs[ICl_3F]$ and $Rb[ICl_3F]$ by the action of iodine trichloride on the alkali fluorides. These belong to the type $M[I_5]$, and presumably have the structure  $\mathrm{I}<^{\mathrm{Cl}}_{\mathrm{Cl}<^{\mathrm{Cl}}_{\mathrm{F}}}$ where the iodine and the linking chlorine have the inert pair. They are of interest as showing that fluorine can form part of a polyhalide ion, but perhaps only when it is a long way from the negative charge.

From the point of view of the inert pair, the question is, what is the lightest halogen which can form the linking atom in a polyhalide ion? There is no doubt that bromine can do this; whether the same can be said of chlorine is less certain. The evidence for the existence of $[Cl_3]'$ is not satisfactory; but we may perhaps accept the above formulation of Booth's compounds as making it probable.

When we come to the neutral inter-halogen compounds (see below, p. 128) there is no doubt that the pair can be inert in chlorine; chlorine trifluoride, ClF_3, is a perfectly definite though very reactive substance (m. p. $-83°$, b. p. $+13°$).

We can sum up our knowledge of the occurrence of the inert pair of electrons as follows:

(1) It is never found except in the sub-typical (second short period) and B elements.

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[10] R. W. G. Wyckoff, *J. Amer. Chem. Soc.*, 1920, **42**, 1100; *A.*, 1920, ii, 489.

[11] H. S. Booth, C. F. Swinehart, and W. C. Morris, *J. Amer. Chem. Soc.*, 1932, **54**, 2561; *J. Physical Chem.*, 1932, **36**, 2779; *A.*, 1932, 823, 1219.

(2) In every group it becomes more stable as the atomic weight and number increase.

(3) As we pass from the earlier groups to the later, we find that it extends to lighter elements.

The limits of its occurrence are marked by the line in the table.

Occurrence of the inert pair of electrons.

Be	B	C	N	O	F
Mg	Al	Si	P	S	Cl
Zn	Ga	Ge	As	Se	Br
Cd	In	Sn	Sb	Te	I
Hg	Tl	Pb	Bi		

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7. THE INTER-HALOGEN COMPOUNDS.

Eleven compounds of the halogens with one another have now been described. Some of these have been known almost as long as the halogens themselves, but several have only recently been discovered, largely through the work of Ruff and his collaborators. None is known which contains more than two different halogens, and all those which have more than two atoms in the molecule are of the type AB_n, in which B is either fluorine or chlorine, and n is 3, 5, or 7; it is evident that all the B atoms are directly joined to A. The valency group of A in the various types is therefore :

Type.	AB.	AB_3.	AB_5.	AB_7.
Valency group of A	6, $\underline{2}$	(2) 2, $\underline{6}$	(2) $\underline{10}$	$\underline{14}$

It will be seen that in AB_3 and AB_5 the atom A has an inert pair of electrons (see p. 127), and that a molecule AB_7 is only possible when A is iodine, since chlorine and bromine are limited by the covalency rule to a covalency of 6.

Type AB.

These compounds are obviously of the same type as the free halogens themselves. Of the six possible compounds, all are known except iodine monofluoride, which is probably too unstable to exist, since bromine monofluoride is highly unstable. Their boiling and melting points (the latter in parentheses) are given in Table I, along with those of the elementary halogens.

Chlorine monofluoride, ClF.[1] Made by the action of slightly moist chlorine on fluorine, or by heating dry chlorine with fluorine at 250°; the reaction is exothermic and reversible. The compound is almost colourless; it reacts like fluorine, but even more readily.

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[1] O. Ruff *et al.*, *Z. angew. Chem.*, 1928, **41**, 1289; *A.*, 1929, 160; *Z. anorg. Chem.*, 1928, **176**, 258; *A.*, 1929, 40; Ruff and F. Laass, *ibid.*, 1929, **183**, 214; *A.*, 1929, 1226; Ruff and W. Menzel, *ibid.*, 1931, **198**, 375; *A.*, 1931, 912; O. Ruff, F. Ebert, and W. Menzel, *ibid.*, 1932, **207**, 46; *A.*, 1932, 902; Ruff and A. Braida, *ibid.*, 1933, **214**, 81; *A.*, 1130; K. Fredenhagen and O. T. Krefft, *Z. physikal. Chem.*, 1929, **141**, 221; *A.*, 1929, 664.

TABLE I.

Boiling and melting points of the AB *compounds.*

	F.	Cl.	Br.	I.
F	− 188° (− 219°)			
Cl	− 100° (− 156°)	− 33·7° (− 102·3°)		
Br	+ 20° (− 33°)	+ 5° (− 66°)	+ 58·8° (− 7·2°)	
I	—	+ 97·4° (α + 27·2°) (β + 13·9°)	116° (36°)	184° (114°)

Bromine monofluoride, BrF. Owing to its instability this compound was not obtained until this year.[2] Bromine reacts very slowly with fluorine in the gaseous state at 0°, while at 50° the only product of the reaction is bromine trifluoride. By saturating bromine with fluorine at + 10° and fractionating under reduced pressure, the monofluoride was obtained in a nearly pure condition, but it changes continuously into the trifluoride and free bromine. It is a pale red gas, which gives a dark red liquid, and orange crystals like potassium dichromate. It is remarkable that the monofluoride is only slightly soluble in bromine, though BrF, BrF_3, and BrF_5 are all miscible with one another. It is clear that the monofluoride is the first product of the action of fluorine on bromine, but that it changes spontaneously into the other fluorides and bromine. Its marked instability as compared with chlorine monofluoride makes it probable that iodine monofluoride, which has never been prepared, cannot exist.

Bromine monochloride, BrCl. This has a curious history. Balard in 1826 noticed that when bromine is mixed with chlorine the colour diminishes, but this observation was disregarded for a century. Then in 1928 G. M. B. Dobson noticed the same thing when using the mixture as a light filter for observing the ozone bands in the atmosphere, and his conclusion was confirmed by S. Barratt and C. P. Stein[3] with the spectrophotometer. Meanwhile B. J. Karsten[4] in 1907 had worked out the complete phase-rule diagram for both vapour pressures and freezing points of the system bromine–chlorine, and concluded from his results that no compound was formed. All the curves—vapour, liquidus, and solidus, both for vapour–liquid and for liquid–solid equilibrium—proceed continuously from Br_2 to Cl_2 and give no sign of combination. This is, however, compatible with the existence of a compound, if it is partly dissociated and in the solid forms a continuous series of solid solutions with both of its components, which is not improbable in view of the identity of molecular type of the three substances Br_2, BrCl, and Cl_2.

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[2] O. Ruff and A. Braida, *Z. anorg. Chem.*, 1933, **214**, 81; *A.*, 1130.

[3] *Proc. Roy. Soc.*, 1929, **122**, 582; *A.*, 1929, 411.

[4] *Z. anorg. Chem.*, 1907, **53**, 365; *A.*, 1907, ii, 447.

The spectroscopic results of Barratt and Stein were confirmed by L. T. M. Gray and D. W. G. Style;[5] from the fall of intensity of the absorption band of bromine in the visible, it appears that at 20° the equilibrium constant $[BrCl]^2/[Br_2]\cdot[Cl_2]$ is about 5, so that at the ordinary temperature the mixture contains about 80% of BrCl.

Confirmation of the existence of BrCl from another side was obtained by N. H. W. Hanson and T. C. James,[6] who found that a mixture of bromine and chlorine adds on to unsaturated acids and esters much more rapidly than either element separately, and gives a mixture of α-chloro-β-bromo- and α-bromo-β-chloro-compounds. T. W. J. Taylor and L. A. Forscey[7] found the same for the reaction with diazoacetic ester, which gave mainly the chlorobromoacetate; this reaction has the advantage that it is practically instantaneous, and may be supposed to give a true measure of the proportion of BrCl present; on this hypothesis they find the proportion to be 80%, in agreement with the spectroscopic results.

W. Jost[8] has measured spectroscopically the equilibrium in mixtures of bromine and chlorine at different temperatures, and also the rate (of the order of 15″ for the half change) of the reaction. He finds the heat of reaction to be very small, and the heat of activation about 14,000 calories.

According to S. Anwar-Ullah,[9] if chlorine is passed into bromine under water below 18°, a crystalline hydrate $BrCl,4H_2O$ is formed, which is more stable than the hydrate of bromine or chlorine.

Iodine monochloride, ICl. Discovered by Davy and by Gay-Lussac in 1814. It is formed by the combination of the elements, or by the oxidation of an iodide in hydrochloric acid. The phase-rule diagram[10] of the system iodine–chlorine is familiar. Iodine monochloride occurs in two solid forms, α, red, m. p. 27·2°, and β, brown, m. p. 13·9°. They give the same liquid, b. p. 97·4°; there is little dissociation in the vapour even at 100°.[11] Chemically the compound behaves like a mixture of its components; *e.g.*, with water it forms hydrochloric and hypoiodous or iodic acids.

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[5] *Proc. Roy. Soc.*, 1930, **126**, 603; *A.*, 1930, 510.

[6] *J.*, 1928, 1955, 2979.

[7] *J.*, 1930, 2272.

[8] *Z. physikal. Chem.*, 1931, **153**, 143; *ibid.*, [*B*], **14**, 413; *A.*, 1931, 431.

[9] *J.*, 1932, 1176.

[10] W. Stortenbeker, *Rec. trav. chim.*, 1888, **7**, 152; *A.*, 1889, 102; *Z. physikal. Chem.*, 1889, **3**, 11.

Iodine monobromide, IBr. Discovered by Balard; formed by direct combination. The solid looks like iodine and the vapour is dark red. Iodine and bromine form a continuous series of solid solutions, like chlorine and bromine. The heat of reaction and the equilibrium constants have been determined by D. M. Yost, T. F. Anderson, and F. Skoog.[12] They find the reaction to be slightly endothermic. The degree of dissociation at 25° is about 8% in the vapour and about 9% in carbon tetrachloride solution.

Type AB_3.

Three compounds of this type are known, ClF_3, BrF_3, and ICl_3.

Chlorine trifluoride, ClF_3.[13] This is produced by heating chlorine or chlorine monofluoride in excess of fluorine. Colourless gas and solid, pale green liquid; m. p. $-83°$, b. p. $+13°$. It is highly active; it reacts with most substances explosively.

Bromine trifluoride BrF_3.[14] Made from its elements. Colourless gas, liquid, and solid; m. p. 8·8°, b. p. 127°. The heat of evaporation is 10,000 calories, which gives a remarkably high Trouton constant. The values of this constant are: Br_2 23·2; BrF_3 25·3; BrF_5 23·7. These values are all high for non-associated liquids, and that for the trifluoride is almost as high as for an alcohol.

Bromine trifluoride is very reactive and fumes in air; it is, of course, the acid fluoride of bromous acid. Its formation by the spontaneous decomposition of the monofluoride has already been mentioned.

Iodine trifluoride, like the monofluoride, is unknown, and in view of Ruff's work on the heptafluoride may be presumed not to exist.

Iodine trichloride, ICl_3. Discovered by Gay-Lussac in 1814. Formed by direct combination of the elements. Lemon-yellow needles; melts at 101° under its own (dissociation) vapour pressure of 16 atmospheres. The density shows that the vapour is almost wholly $ICl + Cl_2$. It is miscible with iodine in all proportions.

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[11] J. McMorris and D. M. Yost, *J. Amer. Chem. Soc.*, 1932, **54**, 2247; *A.*, 1932, 906.

[12] *J. Amer. Chem. Soc.*, 1933, **55**, 552; *A.*, 351.

[13] O. Ruff and H. Krug, *Z. anorg. Chem.*, 1930, **190**, 270; *A.*, 1930, 878; Ruff, F. Ebert, and W. Menzel, *ibid.*, 1932, **207**, 46; *A.*, 1932, 902.

[14] P. Lebeau, *Compt. rend.*, 1905, **141**, 1018; *A.*, 1906, ii, 80; *Ann. Chim. Phys.*, 1906, [viii], **9**, 248; E. B. R. Prideaux, *J.*, 1906, **89**, 316; O. Ruff *et al.*, *Z. anorg. Chem.*, 1932, **206**, 59; O. Ruff and A. Braida, *ibid.*, 1933, **214**, 91; *A.*, 1130.

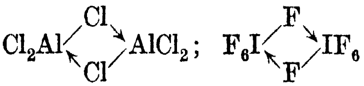
Type AB_5.

Bromine pentafluoride, BrF_5.[15] Obtained by heating bromine trifluoride with fluorine at 200°. Colourless liquid; m. p. — 61·3°, b. p. + 40·5°. Very reactive.

Iodine pentafluoride, IF_5. Obtained first by G. Gore [16] by the action of iodine on silver fluoride; prepared by H. Moissan by the direct combination of the elements.[17] It is a colourless heavy liquid, m. p. — 8°, b. p. 97°. Dissolves iodine and bromine, and fumes in the air, being converted by water into hydrogen fluoride and iodic acid.

Type AB_7.

Iodine heptafluoride, IF_7. This remarkable substance was prepared by Ruff in 1930.[18] It is made by acting with fluorine on the pentafluoride at 270—300°, and fractionating the product. It forms white crystals, which melt at + 5—6° and boil at 4·5°. The heat of evaporation is 7,300 cals., which gives a Trouton constant of 26·4, the same value as for an alcohol, which suggests polymerisation in the liquid. The vapour density of the gas is that required for IF_7. It is not improbable that it should polymerise to some extent in the liquid; it is the only known neutral binary compound with a covalency of 7, and presumably is very ready to increase this to the more stable 8, which it could do by co-ordination to $F_6I{-}F{\rightarrow}IF_7$; it is even possible that it may form a chelate ring, like aluminium or ferric chloride.



It is absorbed (rather slowly) by water to give periodic acid; most substances are as readily attacked by it as by chlorine trifluoride and even more vigorously. N. V. S.

N. V. SIDGWICK.
W. WARDLAW.
R. WHYTLAW-GRAY.

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[15] O. Ruff and W. Menzel, *Z. anorg. Chem.*, 1931, **202**, 49; *A.*, 1932, 133.

[16] *Phil. Mag.*, 1871, [iv], **41**, 309.

[17] *Compt. rend.*, 1902, **135**, 563; see also Prideaux, *J.*, 1906, **89**, 316.

[18] O. Ruff and R. Keim, *Z. anorg. Chem.*, 1930, **193**, 176; *A.*, 1930, 1390.

ORGANIC CHEMISTRY.

PART I.—ALIPHATIC DIVISION.

Acetylenes, Olefin-acetylenes and Allenes.

THE discovery of a convenient means of preparing vinyl- and divinyl-acetylene by the polymerisation of acetylene[1] has given an impetus to the investigation of acetylenic behaviour as it appears both in simple acetylenes and in olefin-acetylenes. A specially interesting feature of work on the latter group is the light that is thrown on the formation and reactivity of allenic systems ($\cdot C{=}C{=}C\cdot$) and on the reactivity of such systems when associated with additional unsaturated units.

Metallic and Organo-metallic Derivatives.—The mercury derivatives of monoalkyl- and monoaryl-acetylenes are formed by the action of potassium mercuri-iodide (K_2HgI_4) or mercuric cyanide and potassium hydroxide on the hydrocarbons. These compounds of the general formula $Hg(C{\vdots}CR)_2$ are crystalline substances of sharp melting point which are suitable for the characterisation of the hydrocarbons.[2, 3] Sodium vinylacetylide, $CH_2{:}CH{\cdot}C{\vdots}CNa$, formed by the action of sodium or sodamide on vinylacetylene, is a reactive powder which can be employed for introducing the vinylacetylenic group into organic compounds; when the sodium derivative is formed in the presence of a ketone (or less satisfactorily an aldehyde), vinylethinylcarbinols, $CH_2{:}CH{\cdot}C{\vdots}C{\cdot}C(OH)R_2$, are produced.[4] The formation of crystalline bis-organomercuric acetylides by passing acetylene into an alkaline solution of alkyl- or aryl-magnesium halides ($C_2H_2 + RHgX \longrightarrow RHgC{\vdots}CHgR$) affords a valuable means for the identification of the latter group of substances; but although the bis-derivatives are the only isolable products of reaction, the mono-acetylides, $RHg{\cdot}C{\vdots}CH$, appear to be formed in solution when an excess of acetylene is employed.[5] Monosubstituted acetylenes appear to react in a similar way to acetylene, since vinylacetylene yields with ethylmagnesium bromide, vinylethinylmagnesium bromide, $CH_2{:}CH{\cdot}C{⋮}CMgBr$—a compound which reacts with acetone and with carbon dioxide in the manner normal to organomagnesium halides, but falls far short of the high degree of reactivity towards alkyl and aryl halides which is displayed by sodium vinylacetylide ($CH_2{:}CH{\cdot}C{⋮}CNa \xrightarrow{RX} CH_2{:}CH{\cdot}C{⋮}CR$).[6]

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[1] *Ann. Reports*, 1932, **29**, 112.

[2] T. H. Vaughn, *J. Amer. Chem. Soc.*, 1933, **55**, 3453; *A.*, 1033.

[3] W. H. Carothers, R. A. Jacobson, and G. J. Berchet, *ibid.*, p. 4206.

[4] W. H. Carothers and R. A. Jacobson, *ibid.*, p. 1097; *A.*, 485.

[5] R. J. Spahr, R. R. Vogt, and J. A. Nieuwland, *ibid.*, pp. 2465, 3728; *A.*, 815, 1177.

Halogenoacetylenes.—Acetylene and sodium acetylide react with iodine dissolved in anhydrous liquid ammonia to give almost theoretical yields of di-iodoacetylene. Certain alkyl- and aryl-acetylenes, $R{\cdot}C{⋮}CH$, also react satisfactorily at —34° with the same reagent to give iodo-derivatives, but others react only at a higher temperature and with reduced yield; the sodium derivatives of the monosubstituted acetylenes, however, are iodinated instantly in liquid ammonia.[7] α-Chloro- and α-bromo-vinylacetylenes, $CH_2{:}CH{\cdot}C{⋮}CX$, are obtainable as distillable liquids by the direct action of chlorine and bromine on bisvinylethinylmercury.[3] A very valuable general method, however, for the preparation of halogeno-derivatives from acetylenic compounds which retain one or more reactive hydrogen atoms consists in submitting the acetylenic compound to the action of alkali hypoiodite, hypobromite, or hypochlorite. By this means dichloro- and dibromo-acetylene, chloro- and bromo-propiolic acid, the α-halogeno-derivatives of numerous Δ^{α}-acetylenic alcohols [8] and of vinylacetylene,[9] and the dihalogeno-derivatives of diacetylene [10] have been successfully obtained.

Additive Reactions.—The hydration of primary acetylenic alcohols, $R{\cdot}C{⋮}C{\cdot}CH_2{\cdot}OH$, or the corresponding acetates by means of mercuric acetate solution results in the addition of the elements of water at the acetylenic bond in one direction only. Thus only the ketones $R{\cdot}CO{\cdot}CH_2{\cdot}CH_2{\cdot}OH$ (or their dehydration products, $R{\cdot}CO{\cdot}CH{:}CH_2$) are formed.[11] When substituted divinylacetylenes are hydrated by means of sulphuric acid–acetic acid, not only is the acetylenic bond affected, but further hydration, leading to cyclisation, occurs.

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[6] W. H. Carothers and G. J. Berchet, *J. Amer. Chem. Soc.*, 1933, **55**, 1094; *A.*, 485; W. H. Carothers and R. A. Jacobson, *ibid.*, p. 1622; *A.*, 590.

[7] T. H. Vaughn and J. A. Nieuwland, *ibid.*, p. 2150; *A.*, 694; *J.*, 1933, 741; *A.*, 930.

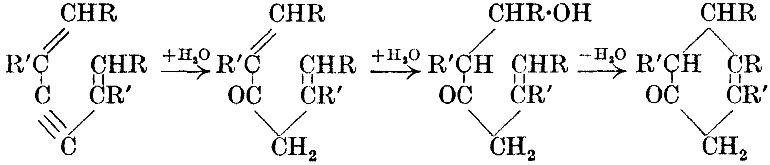
[8] F. Straus, L. Kollek, and W. Heyn, *Ber.*, 1930, **63**, [*B*], 1868; *A.*, 1930, 1157.

[9] R. A. Jacobson and W. H. Carothers, *J. Amer. Chem. Soc.*, 1933, **55**, 4667.

[10] F. Straus, L. Kollek, and H. Hauptmann, *Ber.*, 1930, **63**, [*B*], 1886; *A.*, 1930, 1158.

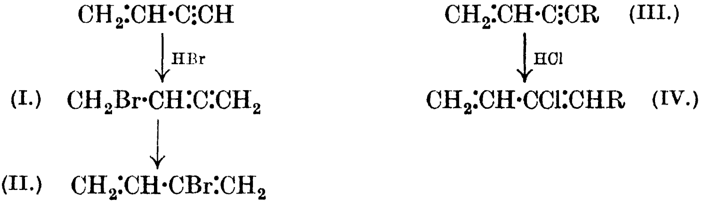
[11] E. D. Venus-Danilova and S. N. Danilov, *J. Gen. Chem.* (*U.S.S.R.*), 1932, **2**, 645; *A.*, 1933, 161.

In this way tetra-alkyl-divinylacetylenes, $CHR{:}CR'{\cdot}C{\vdots}C{\cdot}CR'{:}CHR$ pass into tetra-alkyl*cyclo*hexenes, the stages being presumably : [12]



Hydration of vinylacetylene occurs with mercuric acetate solution at 60—70° : here, however, it is suggested that the additive reaction involves the breaking of only one of the bonds of the triple linkage (instead of two as normally occurs with acetylenes), thereby yielding an olefinic mixed salt, $CH_2{:}CH{\cdot}C(O{\cdot}Hg{\cdot}OAc){:}C(Hg{\cdot}OAc)_2$.[13]

Addition of liquid hydrogen bromide to vinylacetylene [13] yields, as does concentrated hydrochloric acid,[14] an allenic derivative (I) by terminal addition. This derivative readily suffers $\alpha\gamma$-change, to yield (II). When, however, concentrated hydrobromic acid (aq.) is employed as the additive reagent, the re-arranged bromide (II) is obtained directly.[15] Addition of hydrochloric acid to α-alkylacetylenes (III) yields in each of the cases examined an $\alpha\beta$-derivative (IV).[16] The course followed in the reaction between hydrochloric acid (aq.) and divinylacetylene is difficult to establish, since the monohydrochloride reacts with the reagent more rapidly than does the hydrocarbon. There is some ground for supposing that the first reaction product has the allenic constitution (V).[17] This mode of reaction, however, is unlike any other addition of hydrogen halide to conjugated compounds yet described in that (*a*) the hydrogen atom does not unite at a


$CH_2{:}CH{\cdot}C{\vdots}CH$
HBr
(I.)
$CH_2Br{\cdot}CH{:}C{:}CH_2$
(II.)
$CH_2{:}CH{\cdot}CBr{:}CH_2$
$CH_2{:}CH{\cdot}C{\vdots}CR$
(III.)
HCl
$CH_2{:}CH{\cdot}CCl{:}CHR$
(IV.)

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[12] A. T. Blomquist and C. S. Marvel, *J. Amer. Chem. Soc.*, 1933, **55**, 1655; *A.*, 591; D. T. Mitchell and C. S. Marvel, *ibid.*, p. 4276; *A.*, 1270.

[13] W. H. Carothers and G. J. Berchet, *ibid.*, p. 2807; *A.*, 930.

[14] *Ann. Reports*, 1932, **29**, 109.

[15] W. H. Carothers, A. M. Collins, and J. E. Kirby, *J. Amer. Chem. Soc.*, 1933, **55**, 786; *A.*, 371.

[16] W. H. Carothers and R. A. Jacobson, *ibid.*, p. 1624; *A.*, 590.

[17] D. D. Coffman, J. A. Nieuwland, and W. H. Carothers, *ibid.*, p. 2048; *A.*, 694.

terminal carbon atom of the olefin–acetylene system, and (*b*) αδ-addition occurs in an extended conjugated chain despite the fact that such addition has not yet been observed to occur in a conjugated hexatriene or in any other conjugated polyolefin, and that migration of the halogen atom from the position assigned (αγ-change) would yield a stable conjugated chloro-triene.

$$\begin{tikzcd}
CH_2{:}CH\cdot C{:}C\cdot CH{:}CH_2 \arrow[r, "Cl_2"] \arrow[d, "HCl"', "(\alpha\delta\text{-addition})"] & CH_2Cl\cdot CH{:}C{:}CCl\cdot CH{:}CH_2 \quad \text{(VI.)} \\
\underset{\text{(V.)}}{CH_2Cl\cdot CH{:}C{:}CH\cdot CH{:}CH_2} & \underset{\text{(VII).}}{C_7H_7\cdot S\cdot CH_2\cdot CH_2\cdot C{:}C\cdot CH_2\cdot CH_2\cdot S\cdot C_7H_7}
\end{tikzcd}$$

An allenic product (VI) results from the interaction of chlorine with divinylacetylene,[18] but it is impossible to state with certainty whether it arises by direct αδ-addition or by αβ- or αζ-addition, followed by αβ-rearrangement. It is not improbable that αδ-addition may be a common mode of reaction in conjugated olefin–acetylenes such as divinylacetylene, since the δ-halogen atom of the addition product then occurs in an allenic system—a fact which presumably restricts its mobility and therefore precludes further rearrangement.[19] It is to be observed, however, that migration of the α-chlorine atom, which would yield a fully conjugated system, does not occur, although the analogous system, $CH_2{:}C{:}CH\cdot CH_2Cl$, re-arranges with great ease.

Remarkably enough, divinylacetylene reacts towards thiocresol as an unconjugated diolefin, the reagent adding at the ethylenic linkages of the vinyl groups as shown in (VII).[20]

The mode of chlorine addition to α-chloromethylallene, $CH_2{:}C{:}CH\cdot CH_2Cl$, is the one which would be expected, *i.e.*, addition can occur at both double bonds, to give a mixture of

$$CH_2{:}CCl\cdot CHCl\cdot CH_2Cl$$

and $CH_2Cl\cdot CCl{:}CH\cdot CH_2Cl$; it is of interest, however, that the ratio of the products varies considerably with the temperature of reaction.[21] In vinylallene systems such as those represented in (VIII) and (IX) there is no uniform tendency for an addendum to be added at the ends of the conjugated system present in each, since, although in one of four such examples examined, *viz.*, (VIII), chlorine appears to be added at the ends of the conjugated system to give (X), yet in the same example hydrogen chloride is added (almost certainly as the primary reaction) at one of the allenic double bonds to give (XI).[18] In the case of (IX), there is reason to believe that hydrogen chloride is added at the ends of the conjugated system to give (XII).[17]

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[18] D. D. Coffman and W. H. Carothers, *J. Amer. Chem. Soc.*, 1933, **55**, 2040; *A.*, 694.

[19] The tendency to form a completely conjugated system does not appear to be sufficient to bring about αγ-change in the dihydrochloride of divinylacetylene, $CH_2Cl\cdot CH{:}CH\cdot CCl_2\cdot CH{:}CH_2$, also.

[20] W. H. Carothers, *J. Amer. Chem. Soc.*, **1933**, **55**, 2008; *A.*, 695.

[21] W. H. Carothers and G. J. Berchet, *ibid.*, p. 1628; *A.*, 590.

(VIII.) $CH_2Cl{\cdot}CH{:}C{:}CCl{\cdot}CH{:}CH_2$ $CH_2Cl{\cdot}CH{:}C{:}CH{\cdot}CH{:}CH_2$ (IX.)

$CH_2Cl{\cdot}CH{:}CCl{\cdot}CCl{:}CH{\cdot}CH_2Cl$ (X.) $CH_2Cl{\cdot}CH{:}CCl{\cdot}CH{:}CH{\cdot}CH_3$ (XII.)

$CH_2Cl{\cdot}CH{:}CH{\cdot}CCl_2{\cdot}CH{:}CH_2$ (XI.)

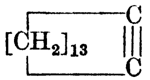
In connexion with the well-known ability of diazomethane to add to Δ^{α}-olefinic and acetylenic esters, K. von Auwers and O. Ungemach [22] draw the conclusion that, although in the pyrazoline derivatives formed from olefinic esters the diazo-group of the reagent is customarily attached to the α-carbon atom of the ester, yet in the formation of pyrazole derivatives from acetylenic esters of the type $RC{:}C{\cdot}CO_2R$, the diazo-group becomes attached to the α-carbon atom if R = alkyl, but to either the α- or the β-carbon atom if R = aryl.

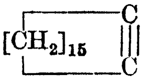
Reactions and Syntheses.—Application of selenium dioxide to the oxidation of simple alkylacetylenes has shown that oxidative attack occurs at the γ-carbon atoms of the latter, n-Δ^{α}-heptinene thus giving n-Δ^{α}-heptinen-γ-ol and n-Δ^{α}-octinene giving n-Δ^{α}-octinen-γ-ol.[23] An interesting synthesis of acetylenic bases of the type $RC{:}C{\cdot}CH_2{\cdot}NR_2$ has been carried out by combining various arylacetylenes with formaldehyde and a secondary amine, according to the equation:

$$RC{:}CH + CH_2O + NHR_2 \longrightarrow RC{:}C{\cdot}CH_2{\cdot}NR_2 + H_2O$$ [24]

By the successive action of bromine and alcoholic potash on *cyclo*pentadecene and *cyclo*heptadecene L. Ruzicka and his collaborators have obtained the 15- and 17-membered cyclic acetylenes, (XIII) and (XIV).[25]

(XIII.)





(XIV.)

Catalytic Hydrogenation.

Much new information has been gained concerning the application of catalysts to the promotion of different varieties of reductive change. The new observations relate to (a) the specificity, (b) the selectivity, and (*c*) the conditions affecting both the specificity and the selectivity of catalyst action.

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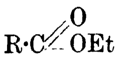
[22] *Ber.*, 1933, **66**, [*B*], 1205; *A.*, 1171.

[23] R. Truchet, *Compt. rend.*, 1933, **196**, 706; *A.*, 486.

[24] C. Mannich and F. T. Chang, *Ber.*, 1933, **66**, [*B*], 418; *A.*, 387.

[25] L. Ruzicka, M. Hürbin, and H. A. Boekenoogen, *Helv. Chim. Acta*, 1933, **16**, 498; *A.*, 599.

The cleavage of oxygenated compounds with simultaneous addition of hydrogen has at various times been observed to occur during catalytic hydrogenation. Such cleavage is not confined to the $>C-O$ linkage, but occurs also at $>C-C<$ linkages. The employment recently of high pressures of hydrogen, and especially of a copper–chromium oxide catalyst in place of the nickel and platinum catalysts previously used, has extended the field of operation and utility of this type of change, which is in its nature hydrogenolysis—strictly analogous to hydrolysis ($\geqslant C{-}O{-} \xrightarrow{H_2} \geqslant CH + HO{-}$; $\leqslant C{-}C \geqslant \xrightarrow{H_2} \geqslant CH + HC \leqslant$).[26] It is found that the linkages indicated by the dotted lines in formulæ (XV) to (XXI) are all susceptible of hydrogenolysis in the presence of copper–chromium oxide at elevated temperatures and pressures (120° to 250°; 140—210 atm.) and to this list must be added a large number of open-chain and cyclic glycols, β-hydroxy-esters, malonic and acetoacetic esters, and other compounds which have been observed to suffer



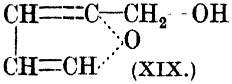
$R\cdot C(=O)\cdots OEt$

(XV.)

$HO\cdots CHR\cdot CH_2\cdot CO_2Et$ (XVI.)

$Ph\cdot CHR\cdots OH$ (XVII.)

$Ph\cdot CHR\cdot CH_2\cdots OH$ (XVIII.)



(XIX.)

$CHMe(OH)\cdots CMe_2\cdot CO_2Et$ (XX.)

$Ph\cdot CH_2\cdots CHPh_2$ (XXI.)

fission at C–O or C–C linkages in the presence of the same catalyst. Certain structural features recognisably affect the ease (*i.e.*, the temperature and rate) of fission at these linkages and determine the course of reaction when the two types of cleavage are in competition; the results, however, apply to certain specified conditions of reaction and cannot be assumed to afford direct evidence concerning the relative strengths of the linkages in various molecules.

The hydrogenolysis of saturated alcohols occurs smoothly in the presence of nickel at 250°/100—200 atm. *n*-Dodecyl, *n*-tetradecyl, *n*-octadecyl, and γ-*cyclo*hexylpropyl alcohols suffer almost quantitative scission at the terminal carbon atoms of the molecules, according to the equation: $R\cdot CH_2\cdot OH + 2H_2 \longrightarrow RH + CH_4 + H_2O$.[27] The reaction applies moreover to secondary alcohols such as *cyclo*hexanol and octan-β-ol, which yield *cyclo*hexane and *n*-octane respectively, and also to diols such as decan-ακ-diol and octadecan-

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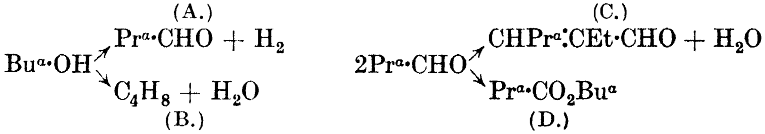
[26] R. Connor and H. Adkins, *J. Amer. Chem. Soc.*, 1932, **54**, 4678; *A.*, 1933, 143.

[27] H. Adkins, C. E. Kommes, E. F. Struss, and W. Dasler, *ibid.*, 1933, **55**, 2992; *A.*, 936.

$\alpha\mu$-diol, which yield octane and *n*-heptadecane respectively. When, however, the vapours of saturated alcohols are submitted alone to the action of a copper–chromium oxide catalyst, reaction may follow one or other of two courses according to the existing conditions of temperature and pressure. Dehydrogenation (reaction A) and a little dehydration (reaction B) occur at 300°/1 atm.; whilst at 300—400°/100—300 atm. the aldehydes formed by dehydrogenation suffer either condensation (*i.e.*, aldolisation, followed by dehydration) (reaction C) or ester formation (reaction D); even at 1 atm. pressure ester formation may become important.



$$\mathrm{Bu^{\alpha}{\cdot}OH}\begin{array}{l}\overset{\text{(A.)}}{\nearrow \mathrm{Pr^{\alpha}{\cdot}CHO} + \mathrm{H_2}}\\ \underset{\text{(B.)}}{\searrow \mathrm{C_4H_8} + \mathrm{H_2O}}\end{array} \qquad \mathrm{2Pr^{\alpha}{\cdot}CHO}\begin{array}{l}\overset{\text{(C.)}}{\nearrow \mathrm{CHPr^{\alpha}{:}CEt{\cdot}CHO} + \mathrm{H_2O}}\\ \underset{\text{(D.)}}{\searrow \mathrm{Pr^{\alpha}{\cdot}CO_2Bu^{\alpha}}}\end{array}$$

The formation of aldols from dehydrogenated alcohols is doubtless related to the appearance of aldol derivatives during G. T. Morgan's methanol synthesis. In the production of methanol from carbon monoxide and hydrogen under high pressure by a chromium–manganese oxide catalyst the formation of higher alcohols becomes appreciable if the catalyst contains traces of the alkaline precipitant. The extent of such formation becomes enhanced if catalysts containing rubidium and cæsium hydroxides are employed, and with a chromium–manganese oxide catalyst containing 15% of rubidium, 42% of the carbon is converted into methanol, 38% into other alcohols, and 15% into carbonyl compounds and derived acetals.[28] Probably the higher alcohols are formed by the aldolisation of simple aldehydes, followed by dehydration and hydrogenation; but quite apart from the correctness or otherwise of this view it is clear that aldols and their dehydration products offer, under available conditions of temperature and pressure control, attractive starting materials for the production of a wide variety of alcohols, glycols, aldehydes, and ketones which are not readily obtainable by other means.[29]

A remarkable result recently reported concerns the reduction of ketones by the aid of a platinum–charcoal catalyst which is further activated with palladium.[30] Acetophenone and its homologues in its presence are reduced to ethylbenzene and its homologues (respectively). The carbonyl group, however, of *cyclo*pentanone,

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[28] G. T. Morgan, D. V. N. Hardy, and R. A. Procter, *Chem. and Ind.*, 1932, **51**, 1; *B.*, 1932, 250.

[29] G. T. Morgan and D. V. N. Hardy, *ibid.*, 1933, 518; *A.*, 809.

[30] N. D. Zelinski, K. Packendorff, and L. Leder-Packendorff, *Ber.*, 1933, **66**, [*B*], 872; *A.*, 715.

*cyclo*hexanone, hexahydroacetophenone and its homologues, and of ketones in which it is separated from the benzene nucleus by at least one methylene group, remains unaffected. It thus becomes possible to separate aromatic ketones from cyclic ketones or those which do not contain the carbonyl group in the α-position to the benzene ring. The reduction of the carbonyl group precedes that of the hydroxyl group in benzoin ($Ph{\cdot}CO{\cdot}CHPh{\cdot}OH \longrightarrow OH{\cdot}CHPh{\cdot}CHPh{\cdot}OH \longrightarrow CH_2Ph{\cdot}CH_2Ph$),[30] and the rate of reduction of the carbonyl group to $>CH{\cdot}OH$ in ω-acetyl esters of the type $CH_3{\cdot}CO{\cdot}[CH_2]_n{\cdot}CO_2Et$ ($n = 1$—5) decreases with increase in the value of n (platinum catalyst),[31] whilst that of lævulic esters, $CH_3{\cdot}CO{\cdot}[CH_2]_2{\cdot}CO_2R$, decreases with increase in the size of R.[32] By employment of a palladium–charcoal catalyst in the reduction of dibasic acid chlorides, various yields of aldehydo-monocarboxylic acids are obtained.[33]

Reductive fission of a C–N linkage in certain quaternary ammonium salts has been observed to occur in the presence of a palladium–charcoal catalyst suspended in acetic acid : thus phenylbenzyldimethylammonium chloride yields toluene and dimethylaniline.[34] Another type of reductive fission of great practical interest is that involved in the decomposition of ozonides by hydrogen in the presence of a palladium–calcium carbonate catalyst. For many ozonides this method is free from the disadvantages attending decomposition by water or zinc and acetic acid, and it affords an elegant means of obtaining good yields of aldehydes and dialdehydes from the ozonides of mono- and di-olefinic compounds respectively, provided that suitable conditions of ozonisation are employed and the temperature during hydrogenation is kept reasonably low.[35]

Carbocyclic esters may be reduced either to the alcohol or to the hydrocarbon stage ($R{\cdot}CO{-}\vdots{-}OMe \longrightarrow R{\cdot}CH_2{-}\vdots{-}OH \longrightarrow R{\cdot}CH_3$). Reduction to the latter stage may be effected directly by using a mixture of two catalysts (*viz.*, copper–chromium oxide and nickel); but it is best to conduct the operation in two stages, since the water formed in the second stage prevents completion of the first stage.[36]

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[31] E. J. Lease and S. M. McElvain, *J. Amer. Chem. Soc.*, 1933, **55**, 806; *A.*, 376.

[32] R. W. Thomas, H. A. Schuette, and M. A. Cowley, *ibid.*, 1931, **53**, 3861; *A.*, 1931, 1397.

[33] N. Fröschl, A. Maier, and A. Heuberger, *Monatsh.*, 1932, **59**, 256; *A.*, 1932, 499.

[34] H. Emde, *Helv. Chim. Acta*, 1932, **15**, 1330; *A.*, 1933, 55.

[35] F. G. Fischer, H. Düll, and L. Ertel, *Ber.*, 1932, **65**, [*B*], 1467; *A.*, 1932, 1113.

[36] B. Wojcik and H. Adkins, *J. Amer. Chem. Soc.*, 1933, **55**, 1293; *A.*, 484.

Reduction of ethyl phenylacetate in the presence of a copper-chromium oxide catalyst at 250° yields both the alcohol $Ph{\cdot}CH_2{\cdot}CH_2{\cdot}OH$ and the hydrocarbon $Ph{\cdot}CH_2{\cdot}CH_3$:[37] as the ester gradually disappears from the reaction mixture, the proportion of alcohol to hydrocarbon present in the latter decreases—a result to be expected if the ratio of the products depends only on the relative concentrations of the ester and the alcohol in the mixture. No modification of the catalyst has resulted in the attainment of preferential hydrogenation of the carbethoxyl group as compared with the carbinol group derived therefrom; on the other hand, various substances are found to exercise a deactivating influence on the catalyst, thereby lowering the proportion of alcohol produced. The best yield of alcohol is obtained by interrupting hydrogenation at the point at which 5—10% of unchanged ester remains, but the highest degree of conversion of ester into alcohol (80%) is secured in the earlier stages of the reaction. If desired, reduction of the carbethoxyl group in ethyl phenylacetate and analogous esters may be preceded by hydrogenation of the nucleus: in this case a nickel catalyst is first employed and subsequently a copper-chromium oxide catalyst. In aromatic esters the position of the phenyl group has a marked effect on the ease of scission of the C–O group, but specific effects of this nature disappear with hydrogenation of the nucleus.

Amines are obtainable by the catalytic reduction of oximes ($>C{:}NOH \longrightarrow >C{\cdot}NH_2$). W. H. Hartung and his collaborators reported the preparation of benzylamine and various other amines by hydrogenation of the appropriate oximes in hydrochloric acid solution in the presence of palladium,[38] but no such reduction has hitherto been satisfactorily effected with a nickel catalyst. Good yields of primary amines are, however, reported as procurable from oximes by employing a nickel-kieselguhr catalyst,[39] and in some cases by the use of platinum black.[40] Mandelonitriles are smoothly reduced to amines in the presence of platinum and a slight excess of hydrochloric acid.[41]

Extensive hydrogenolysis of glucose, sorbitol, mannitol, sucrose, lactose, maltose, and related compounds occurs when these substances are hydrogenated over copper–chromium oxide at 250°/300 atm., the products being methyl and ethyl alcohols, propane-αβ-diol, and various hydroxy-hexanes.[42] Hydrogenolytic fission of various ring systems can also be readily effected in the presence of platinum–charcoal at 300°.[43] In contrast to this, all the resources of technique and equipment which have been applied to the reduction of diaminodimesityl and 6 : 6′-dimethoxydiphenic acid have failed to bring about reduction.[44] It is possible that the same factors which prevent the rotation of the rings with respect to each other in these diphenyl derivatives also prevent adsorption of the benzenoid compound by the catalyst and thus inhibit the first step of the reduction process.

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[37] H. Adkins, B. Wojcik, and L. W. Covert, *J. Amer. Chem. Soc.*, 1933, **55**, 1669; *A.*, 604.

[38] *Ibid.*, 1928, **50**, 3370; *A.*, 1929, 184; *ibid.*, 1929, **51**, 2262; *A.*, 1929, 1066; *ibid.*, 1930, **52**, 3317; *A.*, 1930, 1286; *ibid.*, 1931, **53**, 2248; *A.*, 1931, 1057.

[39] C. F. Winans and H. Adkins, *ibid.*, 1933, **55**, 2051; *A.*, 700.

[40] M. Krajčinović and D. Vranjican, *Bull. Soc. chim.*, 1933, [iv], **53**, 145; *A.*, 595.

[41] J. S. Buck, *J. Amer. Chem. Soc.*, 1933, **55**, 2593, 3388; *A.*, 821, 1049. Compare W. H. Hartung, *ibid.*, 1928, **50**, 3370; *A.*, 1929, 184.

With regard to selectivity in hydrogenation, recent experiments show beyond any doubt that, in those cases in which two or more courses of reaction are offered, a large degree of selective discrimination may be exercised by the catalyst. Two main categories of selective phenomena are to be distinguished : (1) relating to examples in which *mixtures* of different mono-olefins, or *mixtures* of two or more substances displaying different types of unsaturation (*e.g.*, mono-olefins, conjugated di- or poly-olefins, acetylenes, allenes), undergo hydrogenation; and (2) relating to examples in which different types or kinds of unsaturation or reducibility occur together within the molecule of substance to be reduced. With regard to the first of these groups it was suggested by S. V. Lebedev and his collaborators[45] as early as 1925 that the main factor which determines preference of reduction (as also rate of reduction of the individual compounds) in mixtures of mono-olefins is the degree of substitution : thus mono-substituted olefinic compounds, whether hydrocarbons or not, are reduced in preference to di-, di- to tri-, and tri- to tetra-substituted compounds; and further, mono-, di-, tri-, and tetra-substituted compounds are reduced at rates which diminish for the respective types in the order cited. Further observations by Lebedev and A. O. Yakubchik indicated that butadienes are reduced in preference to mono-olefinic substances.[46] It is pointed out by E. H. Farmer and R. A. E. Galley[47] that the principle of consecutive (selective) reduction here embodied is rigidly observed in (*a*) various binary mixtures of Δ^{α}-, Δ^{β}-, and Δ^{γ}-olefinic acids which they examined and (*b*) mixtures of butadienoid and mono-olefinic acids. There is, nevertheless, good reason to challenge the generalisation that the order of preferential reduction in mixtures of olefinic substances necessarily runs parallel to the relative speeds of reduction of the pure components, since in mixtures of allyl alcohol and Δ^{α}-hexenoic acid [47] and of pinene and cinnamic acid [48] the component which is reduced the more slowly when each is taken separately is preferentially reduced in the binary mixture.

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[42] W. H. Zartman and H. Adkins, *J. Amer. Chem. Soc.*, 1933, **55**, 4562.

[43] N. D. Zelinski, B. A. Kazanski, and A. F. Plate, *Ber.*, 1933, **66**, [*B*], 1415; *A.*, 1150.

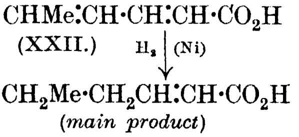
[44] C. R. Waldeland, W. H. Zartman, and H. Adkins, *J. Amer. Chem. Soc.*, 1933, **55**, 4234; *A.*, 1294.

[45] *J.*, 1925, **127**, 418; *A.*, 1925, i, 350.

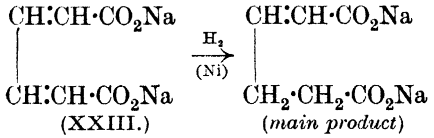
[46] *Ibid.*, 1928, 823, 2190; *A.*, 1928, 613, 1111.

[47] *Ibid.*, 1933, 687; *A.*, 935.

In conjugated butadiene-α-carboxylic esters of the sorbic acid series, reduction may occur selectively at one or other of the double bonds or at the terminals of the butadienoid system. With platinum at room temperature and atmospheric pressure, the dominant mode of reduction for sorbic acid (XXII) is unselective as regards the αβ- and γδ-double bonds of the butadiene system; but such selectivity as exists reveals the γδ-double bond as much more prone to attack than is the αβ-double bond.[47, 49] With an active nickel catalyst, however, recent observations of the reporter [50] show that practically quantitative reduction of sorbic acid to the dihydro-stage can be achieved at room temperature and atmospheric pressure; and in the course of reduction the γδ-double bond is by far the most extensively attacked, but some αδ- and αβ-reduction also occurs. In the case of sodium muconate (XXIII), where both olefinic centres are of αβ-type, 50% hydrogenation gives rise to only



$$\begin{array}{c} CHMe{:}CH{\cdot}CH{:}CH{\cdot}CO_2H \\ \text{(XXII.)} \quad \downarrow H_2\ (Ni) \\ CH_2Me{\cdot}CH_2CH{:}CH{\cdot}CO_2H \\ \textit{(main product)} \end{array}$$



$$\begin{array}{c} CH{:}CH{\cdot}CO_2Na \\ | \\ CH{:}CH{\cdot}CO_2Na \\ \text{(XXIII.)} \end{array} \xrightarrow[(Ni)]{H_2} \begin{array}{c} CH{:}CH{\cdot}CO_2Na \\ | \\ CH_2{\cdot}CH_2{\cdot}CO_2Na \\ \textit{(main product)} \end{array}$$

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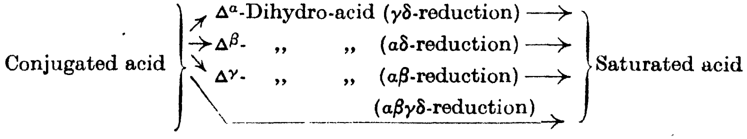
[48] H. Adkins, F. F. Diwoky, and A. E. Broderick, *J. Amer. Chem. Soc.*, 1929, **51**, 3418; *A.*, 1930, 40.

[49] The scheme of reaction is considered to be the following,


Conjugated acid
Δ^{α}-Dihydro-acid ($\gamma\delta$-reduction)
Δ^{β}- ,, ,, ($\alpha\delta$-reduction)
Δ^{γ}- ,, ,, ($\alpha\beta$-reduction)
($\alpha\beta\gamma\delta$-reduction)
Saturated acid

in which complete disappearance of conjugated material is achieved before the ethylenic products begin to suffer reduction. Here there are two types of reaction in competition *at the outset, viz.*, A and B in the scheme: Dihydro-acid $\xleftarrow{A}$ Conjugated acid $\xrightarrow{B}$ Saturated acid ($\alpha\beta\gamma\delta$-addition); reduction of the dihydro-acids does not compete with these. The case differs from that of acetylenic compounds (see below).

[50] Unpublished.

a 50% yield (*ca.*) of dihydro-derivative, which includes some proportion of the Δ^{β}-form. Thus the degree of selectivity exercised by a platinum catalyst (which becomes enhanced by "ageing" of the catalyst) [47] is greatly inferior, under the conditions of experimentation employed, to that exercised by an active nickel catalyst, but to the extent that selective discrimination does occur, the most readily (although not solely) attacked centre in a conjugated butadiene-α-carboxylic acid is for both platinum and nickel the γδ-double bond. The appearance of marked selective action in poly-olefinic systems has obvious synthetic and diagnostic applications.

The difference in catalytic action between platinum and nickel is shown in the hardening of arachis and other oils containing poly-olefinic components. Platinum tends at the ordinary temperature and atmospheric pressure to promote the complete saturation of the unsaturated molecules of these substances; nickel, on the other hand, tends at about 180° and atmospheric pressure to promote selective hydrogenation, resulting in the production of glycerides of oleic acid or of its isomerides.[51] A quite similar difference to the foregoing, however, appears between the products obtained by hardening in the presence of nickel at low pressures and high temperatures and those obtained with nickel at very high pressures (100—300 atm.) and the ordinary temperature: the former tend to be composed of mono-olefinic glycerides and the latter of fully saturated glycerides.[52]

In the case of certain acetylenes S. V. Lebedev and V. J. Schtern [53] report that hydrogenation in the presence of platinum yields ethylenes ($CR{\vdots}CH \xrightarrow{H_2} CHR{:}CH_2$), but these suffer further hydrogenation immediately subsequent to their formation at rates which depend on the nature of the substituent group (R) and on the relative concentrations of the acetylenic and ethylenic components present in the reduction mixture at the time. According to J. S. Salkind and his collaborators [54] the process of hydrogenation of acetylenes proceeds in two stages ($\dot{C}{\equiv}\dot{C} \longrightarrow \dot{C}H{=}\dot{C}H \longrightarrow \dot{C}H_2{\cdot}\dot{C}H_2$) and the relative speeds of the two consecutive reactions vary very considerably with the nature of the substitution in the original acetylenic system. Thus in presence of palladium the first stage of reduction may proceed more or less rapidly than, or at the same rate as, the second, and the result is independent of the mode of preparation and the state of dispersion of the catalyst and of the kind of support-material employed. The relative yield of the ethylenic product of reaction may apparently depend on the velocity of hydrogenation, which in turn is stated to depend on the concentration of the catalyst and on the nature of the solvent employed. Analogous results are reported for platinum, but it is claimed that palladium has, and platinum has not, a special affinity for triple linkages.

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[51] H. I. Waterman, J. A. van Dijk, and C. van Vlodrop, *Rec. trav. chim.*, 1932, **51**, 653; *A.*, 1932, 1018.

[52] H. I. Waterman and (Frl.) M. Zaayer, *ibid.*, p. 401; *A.*, 1932, 601. Compare H. P. Kaufmann and E. H. Schmidt, *Ber.*, 1927, **60**, [*B*], 50; *B.*, 1927, 226.

[53] *J. Gen. Chem.* (*U.S.S.R.*), 1932, **2**, 249; *A.*, 1932, 1231.

[54] *Ibid.*, 1933, **3**, 91; *A.*, 805.

Natural Polyene Pigments (Lipochromes) and Vitamin A.

During the past year, owing mainly to the researches of P. Karrer and R. Kuhn and their numerous collaborators, striking progress has been made in the elucidation of the constitutions of a number of naturally occurring polyene pigments belonging to the group of carotenoids.[55] Pigments of polyene type are widely distributed in the vegetable and animal kingdoms and the group comprises hydrocarbons, alcohols (xanthophylls, phytoxanthins), ketones, carboxylic acids, and carboxylic esters.

In most of these substances there occurs a conjugated C_{20}-chain composed of two double-isoprene skeletons linked together by a double bond (*) to form the system (XXIV).

$$\mathrm{:CH\cdot CMe:}\underbrace{\mathrm{CH\cdot CH:CH\cdot CMe:CH\cdot CH\overset{*}{:}CH\cdot CH:CMe\cdot CH:CH\cdot CH:}}_{\text{Fragment A.}}\mathrm{CMe\cdot CH:} \qquad \text{(XXIV.)}$$

This system, being symmetrical about the double bond, does not consist merely of isoprene units joined end to end, but may be regarded as the middle portion of a still larger symmetrical system containing the fused carbon *skeletons* of two phytol molecules. This larger system is the one which occurs in open-chain form in lycopene (XXV), and in semi-cyclic form in β-carotene (XXVI): it incorporates at each end the C_{13} carbon framework belonging to α- or β-ionone, whilst its middle portion is composed of the conjugated straight-chain fragment designated by **A** in formula (XXIV). For convenience in describing the natural polyenes the system derived from **A** by interchanging the positions of the double and single linkings (*i.e.*, the system which occurs in the terminally reduced derivatives of substances containing **A**, and in at least one of the naturally occurring polyenes) is designated **B**, the saturated system derived by complete hydrogenation of **A** or **B** is

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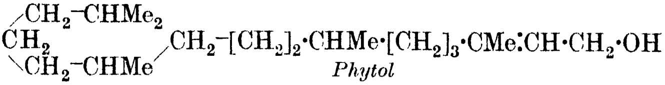
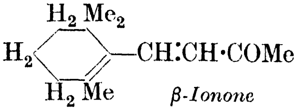
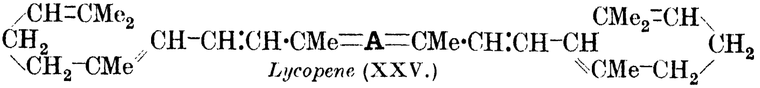
[55] For the history of the carotenoids and the early work on their isolation and characterisation, the reader is referred to P. Karrer, *Z. angew. Chem.*, 1929, **42**, 918; R. Willstätter and Stoll, " Untersuchungen über Chlorophyll," Berlin, 1913; L. S. Palmer, " Carotinoids and Related Pigments," New York, 1922.



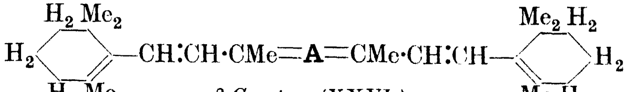
Phytol



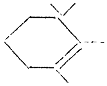
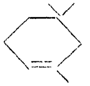
β-Ionone



Lycopene (XXV.)



β-Carotene (XXVI.)

designated **C**, and the trimethyl*cyclo*hexene rings of β- and α-ionone are symbolically represented by  and  respectively.

Thus:

$\mathbf{B} = \cdot CH{:}CH\cdot CH{:}CMe\cdot CH{:}CH\cdot CH{:}CH\cdot CMe{:}CH\cdot CH{:}CH\cdot$

and $\mathbf{C} = \cdot[CH_2]_3\cdot CHMe\cdot[CH_2]_4\cdot CHMe\cdot[CH_2]_3\cdot$

Other natural polyenes contain modifications of the carbon system present in β-carotene, such modifications including hydroxylation or ketonisation of the ionone rings, curtailment of the chain, and replacement of the **A**-system of conjugation by the **B**-system.

Bixin and Crocetin.—Last year it was reported [56] that P. Kuhn and A. Winterstein had suggested a symmetrical formula for bixin, the yellow pigment of the seeds of annatto (*Bixa orellana*), in place of an earlier formula in which the four methyl substituents known to be present in the chain had been assigned unsymmetrical positions in order to allow for the reported non-equivalence of the carboxyl groups. At that time, however, the positions occupied by the methyl groups had not been demonstrated, but the new formulation was of interest in revealing the bixin chain as constituting the middle fragment of the lycopene molecule according to P. Karrer's formulation (XXV) [57] of the latter.

$$HO_2C\cdot CH{:}CH\cdot CMe{:}\mathbf{A}{:}CMe\cdot CH{:}CH\cdot CO_2Me$$

(XXVII.) *Bixin* (K. and W.)

$$HO_2C\cdot CMe{:}\mathbf{A}{:}CMe\cdot CO_2H$$

(XXVIII.) *Crocetin.*

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[56] *Ann. Reports*, 1932, **29**, 120.

[57] *Helv. Chim. Acta*, 1930, **13**, 1084; 1931, **14**, 435; *A.*, 1930, 1422; 1931, 597.

The correctness of the position assigned to the methyl groups, and the symmetry of (chain) constitution, have now been demonstrated by the synthesis of perhydronorbixin (XXIX) [58] by the stages :—

$$\text{Br[CH}_2\text{]}_3\text{Br} \xrightarrow[\text{(Hydrol.)}]{\text{CMeNa(CO}_2\text{Et)}_2} \text{HO}_2\text{C·CHMe·[CH}_2\text{]}_3\text{·CHMe·CO}_2\text{H} \xrightarrow[\text{of ester}]{\text{Reduction}}$$

$$\text{CH}_2\text{(OH)·CHMe·[CH}_2\text{]}_3\text{·CHMe·CH}_2\text{·OH} \xrightarrow[\text{(Hydrol.)}]{\text{PBr}_3\text{; CHNa(CO}_2\text{Et)}_2}$$

$$\text{HO}_2\text{C·[CH}_2\text{]}_2\text{·CHMe·[CH}_2\text{]}_3\text{·CHMe·[CH}_2\text{]}_2\text{·CO}_2\text{H} \xrightarrow[\text{KEt salt (Hydrol.)}]{\text{Electrolysis of}}$$

$$\text{HO}_2\text{C·[CH}_2\text{]}_2\text{·CHMe·}\mathbf{C}\text{·CHMe·[CH}_2\text{]}_2\text{·CO}_2\text{H}$$

Perhydronorbixin (XXIX.)

Not only is the synthetic product identical with that derived by the hydrolysis of catalytically reduced natural bixin, but it is found that when the terminal carboxyl groups of perhydronorbixin are degradatively removed by the ingenious procedure represented in the stages

$$\text{R·CH}_2\text{·CO}_2\text{H} \xrightarrow{\text{Br; KOH}} \text{R·CH(OH)·CO}_2\text{H} \xrightarrow[\text{acid chloride}]{\text{MgMeI on}}$$

$$\text{R·CH(OH)·CMe}_2\text{·OH} \xrightarrow{\text{Pb(OAc)}_4} \text{R·CHO} + \text{Me}_2\text{CO}$$

the product is a dialdehyde, showing clearly that no methyl groups are attached to the α- and α′-carbon atoms of bixin and perhydronorbixin. In this respect perhydronorbixin differs from perhydrocrocetin, since by the same procedure the latter gives a diketone, $C_{18}H_{34}O_2$.

To crocetin, the pigment derived from *Crocus sativus* (saffron), the formula $C_{19}H_{22}O_4$ was originally assigned,[59] but later this was replaced by the formula $C_{20}H_{24}O_4$ in which four of the carbon atoms were almost certainly present as methyl groups.[60] The fact that at least one of the four methyl groups is attached to an α-carbon atom was established by comparative oxidations of dihydro-(terminally reduced)-crocetin and dihydronorbixin, but all uncertainty as to orientation in the carbon chain was dispelled by the production of the above-mentioned diketone, $C_{18}H_{34}O_2$ (actually $\text{Me·CO·[CH}_2\text{]}_3\text{·CHMe·[CH}_2\text{]}_4\text{·CHMe·[CH}_2\text{]}_3\text{·CO·Me}$), and by the synthesis of perhydrocrocetin, $\text{HO}_2\text{C·CHMe·}\mathbf{C}\text{·CHMe·CO}_2\text{H}$, from βζ-dimethylheptane-αη-diol[61] in a manner somewhat similar to that of perhydronorbixin from trimethylene bromide. Any further evidence necessary to the complete establishment of the relationship existing between crocetin and bixin has been amply supplied (1) by the building up of perhydronorbixin synthetically from the ester of perhydrocrocetin[62] and (2) by the degradation of perhydronorbixin to perhydrocrocetin:[63] the former process involves the lengthening of the perhydrocrocetin chain by four CH_2-groups, and the latter the reverse transformation.

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[58] P. Karrer, P. Benz, R. Morf, H. Raudnitz, M. Stoll, and T. Takahashi, *Helv. Chim. Acta*, 1932, **15**, 1218; *A.*, 1932, 1234; *ibid.*, p. 1399; *A.*, 1933, 52. It is remarkable that the synthetic acid is obtained in the same stereo-form as the perhydrogenated acid derived from natural bixin, although the latter possesses no fewer than four asymmetric carbon atoms and can exist in six inactive forms.

[59] P. Karrer and H. Salomon, *ibid.*, 1928, **11**, 711; *A.*, 1928, 869; R. Kuhn, A. Winterstein, and W. Wiegand, *ibid.*, p. 716; *A.*, 1928, 869.

[60] R. Kuhn and F. L'Orsa, *Ber.*, 1931, **64**, [*B*], 1732.

The *cis-trans* nature of the isomerism existing between bixin (α-) and β-bixin was referred to in last year's Report; another variety of bixin, *viz.*, *iso*bixin, reported by J. F. B. van Hasselt[64] to result from exchange of the esterified and the unesterified carboxyl group, has not been obtainable by subsequent workers.[65] An isomeride of crocetin has now been isolated from saffron, and this on account of the extreme ease with which it changes into crocetin and the fact that its dihydro-derivative is identical with dihydrocrocetin, is regarded as a geometrical isomeride of crocetin containing one or more *cis* double bonds.[66] Since ordinary bixin (α-) and crocetin must now be considered to possess *cis*- and *trans*-configurations respectively and β-bixin a *trans*-configuration, there would be no rational significance in designating the new *cis*-isomeride of crocetin β-crocetin: indeed the prefixes α, β-, and γ- have been employed in the past to distinguish between free crocetin and its monomethyl (m. p. 218°) and dimethyl (m. p. 221°) esters.[67] Accordingly the use of the terms *stable* and *labile* (or the numbers I and II) in describing the isomeric bixins and crocetins is suggested.

	M.p.	Geomet. form.	Variety.
β-Bixin	270°	*trans*	stable (I)
Bixin (ordinary)	196	*cis*	labile (II)
α-Crocetin	285	*trans*	stable (I)
Crocetin (new)	141	*cis*	labile (II)

Although crocetin and bixin represent the middle sections of the molecules of carotene and lycopene, the suggestion that they are derived in the plant by the oxidative degradation of carotenoid substances[68] has not remained uncriticised.[65] Interesting evidence on this point is afforded by the recent discovery that picrocrocin $(C_{16}H_{26}O_7)$, the bitter principle of saffron, yields on hydrolysis equimolecular quantities of saffronal (a cyclic aldehyde of constitution XXX) and glucose, so that picrocrocin is a (β-)glucoside of hydrated saffronal, probably having the constitution (XXXI).[69]

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[61] P. Karrer, F. Benz, and M. Stoll, *Helv. Chim. Acta*, 1933, **16**, 297; *A.*, 594.

[62] P. Karrer and F. Benz, *ibid.*, p. 337; *A.*, 594.

[63] H. Raudnitz and J. Peschel, *Ber.*, 1933, **66**, [*B*], 901; *A.*, 807.

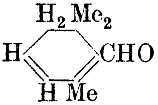
[64] *Rec. trav. chim.*, 1911, **30**, 1; *A.*, 1911, i, 550.

[65] P. Karrer and T. Takahashi, *Helv. Chim. Acta*, 1933, **16**, 287; *A.*, 594.

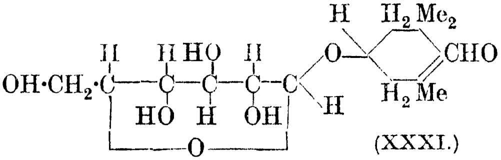
[66] R. Kuhn and A. Winterstein, *Ber.*, 1933, **66**, [*B*], 209; *A.*, 258.

[67] P. Karrer and H. Salomon, *Helv. Chim. Acta*, 1927, **10**, 397; *A.*, 1927, 571; *ibid.*, 1928, **11**, 513; *A.*, 1928, 644.

[68] R. Kuhn and C. Grundmann, *Ber.*, 1932, **65**, [*B*], 1880; *A.*, 1933, 142.



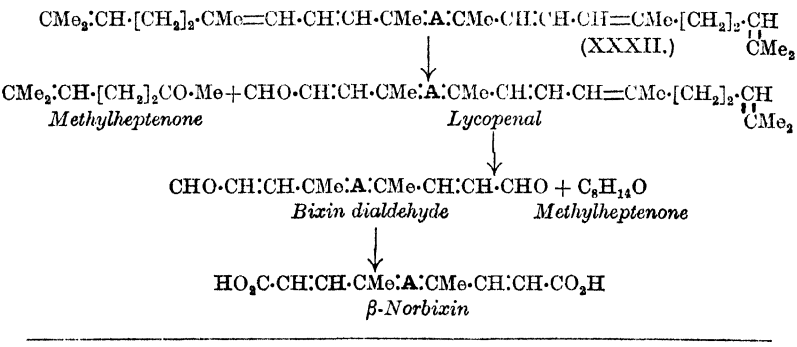
(XXX.)
Saffronal



(XXXI.)
Picrocrocin

Now in view of the facts (1) that in saffron large proportions of glycosidically-linked *trans*- and *cis*-crocetin occur in the form of crocin side by side with smaller proportions of lycopene, β- and γ-carotene and zeaxanthin, and (2) that the framework of 2 mols. of saffronal and 1 mol. of crocetin together make up the framework of a dicyclic C_{40}-carotenoid pigment, it appears that such dicyclic carotenoids suffer oxidative scission of the terminal ring systems and that the two varieties of scission product so formed become glucosidically combined to yield picrocrocin and crocin respectively. This hypothesis is fortified by the observation that the proportion of these two substances in fresh saffron is 1·4 : 1.

Lycopene and the Carotenes.—Lycopene, which occurs as a red colouring matter in the berries of bitter-sweet and of other plants, and in rose-hips and tomatoes, has the empirical formula $C_{40}H_{56}$.[70] Since it contains thirteen double bonds, as indicated by hydrogenation and halogenation tests, P. Karrer and his collaborators proposed the formula (XXXII) on the assumption that its double



$$\mathrm{CMe_2{:}CH{\cdot}[CH_2]_2{\cdot}CMe{=}CH{\cdot}CH{:}CH{\cdot}CMe{:}A{:}CMe{\cdot}CH{:}CH{\cdot}CH{=}CMe{\cdot}[CH_2]_2{\cdot}\underset{\underset{CMe_2}{\|}}{CH}}$$

(XXXII.)

$$\downarrow$$

$$\mathrm{CMe_2{:}CH{\cdot}[CH_2]_2CO{\cdot}Me + CHO{\cdot}CH{:}CH{\cdot}CMe{:}A{:}CMe{\cdot}CH{:}CH{\cdot}CH{=}CMe{\cdot}[CH_2]_2{\cdot}\underset{\underset{CMe_2}{\|}}{CH}}$$

Methylheptenone *Lycopenal*

$$\downarrow$$

$$\mathrm{CHO{\cdot}CH{:}CH{\cdot}CMe{:}A{:}CMe{\cdot}CH{:}CH{\cdot}CHO + C_8H_{14}O}$$

Bixin dialdehyde *Methylheptenone*

$$\downarrow$$

$$\mathrm{HO_2C{\cdot}CH{:}CH{\cdot}CMe{:}A{:}CMe{\cdot}CH{:}CH{\cdot}CO_2H}$$

β-Norbixin

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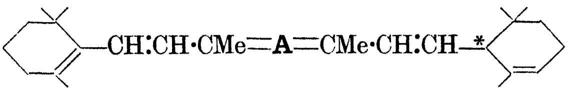
[69] R. Kuhn and A. Winterstein, *Naturwiss.*, 1933, **28**, 527; *A.*, 954.

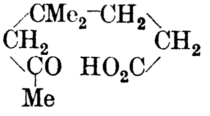
[70] R. Willstätter and H. H. Escher, *Z. physiol. Chem.*, 1910, **64**, 47; *A.*, 1910, i, 330.

bonds were symmetrically disposed and that it was built up from two phytol residues.[71] The fission of the lycopene chain by chromic acid to yield first lycopenal [72] and then bixin dialdehyde,[68] the latter of which is convertible into the corresponding dibasic acid, establishes at once the correctness of Karrer's formula, since the dibasic acid proves to be identical with the hydrolysed geometrical isomeride of ordinary bixin, *i.e.*, β-norbixin or *cis*-norbixin.

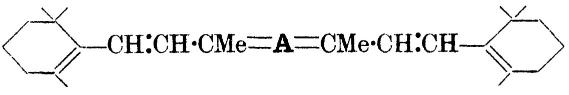
Carotene is obtained from numerous sources: optically active preparations may be obtained from carrot, palm oil, *Sorbus aucuparia*, *Aesculus hippocastanum*, and inactive preparations from winter spinach, grass, and stinging nettle.[73] Carotene has been found to contain three distinct substances, of which two (α- and β-carotene) contain eleven double bonds and, like vitamin A, promote growth. α-Carotene, m. p. 187° (corr.), is optically active and can be completely separated from β-carotene by filtration of its ligroin solution through calcium hydroxide or lime, the β-form being adsorbed in the dark reddish-brown upper layer and the α-form in the lower yellow layer (Tswett's method of chromatographic analysis). The two forms differ in melting point, solubility, and optical activity and in the position of their absorption bands.[74] Now, since α-carotene yields by ozonolysis *both* geronic acid and *iso*geronic acid, its constitution is without doubt correctly represented by (XXXIII).[75]



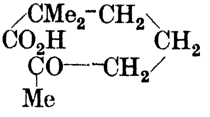
a-Carotene (XXXIII.)



iso*Geronic acid*



β-Carotene (XXXIV.)



Geronic acid

For β-carotene, m. p. 183° (corr.), Karrer and his collaborators proposed the symmetrical formula (XXXIV), although at the time less than one molecular proportion of geronic acid had been derived from it by oxidation.[76] Careful thermal degradation of β-carotene yielded toluene and *m*-xylene, which doubtless arose by cyclisation of fragments of the polyene chain (:CH·CH:CH·CMe:CH·CH: and :CH·CMe:CH·CH:CH·CMe:). It was known, however, that zeaxanthin, whose constitution (according to the evidence available) differed from the proposed one for β-carotene only by the presence of hydroxyl groups in the ionone rings, yielded not only toluene and *m*-xylene but also a small proportion of 2 : 6-dimethylnaphthalene. β-Carotene, on testing, was found also to yield 2 : 6-dimethylnaphthalene. But there is plain evidence that vitamin A, which stands biologically and chemically close to β-carotene (see p. 159), yields by cyclisation and dehydrogenation, not 2 : 6-, but 1 : 6-dimethylnaphthalene; furthermore, the 1 : 6-compound might well be expected to arise by the cyclisation and dehydrogenation of a β-ionone ring and its adjacent carbon atoms. Consequently the formation of 2 : 6-dimethylnaphthalene by thermal degradation probably arises in the manner

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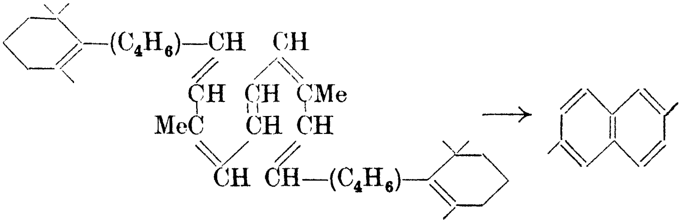
[71] *Ann. Reports*, 1932, **29**, 122.

[72] R. Kuhn and C. Grundmann, *Ber.*, 1932, **65**, [*B*], 898; *A.*, 1932, 749.

[73] R. Kuhn and E. Lederer, *Ber.*, 1931, **64**, [*B*], 1349; *A.*, 1931, 959; *Z. physiol. Chem.*, 1931, **200**, 246; *A.*, 1931, 1421.

[74] P. Karrer and O. Walker, *Helv. Chim. Acta*, 1933, **16**, 641; *A.*, 805; P. Karrer, O. Walker, K. Schöpp, and R. Morf, *Nature*, 1933, **132**, 26; *A.*, 805.

[75] P. Karrer, R. Morf, and O. Walker, *Helv. Chim. Acta*, 1933, **16**, 975; *A.*, 1150; compare P. Karrer, A. Helfenstein, H. Wehrli, and A. Wettstein, *ibid.*, 1930, **13**, 1084; *A.*, 1930, 1422; P. Karrer and R. Morf, *ibid.*, 1931, **14**, 1033; *A.*, 1931, 1299.



and this probability is rendered almost a certainty by the fact that *trans*-crocetin, which contains no carbon rings, has now been found to yield 2 : 6-dimethylnaphthalene. In this case a large part (12 carbon atoms) of the conjugated chain of β-carotene must be identical (although not necessarily as regards geometrical configuration) with that of crocetin.

Further striking testimony to the correctness of Karrer's formulation of β-carotene is supplied by the fact that the substance can be oxidised in two stages to yield first a diketone (XXXV) by the fission of one ring [77] and then a tetraketone (XXXVI) by the fission of both.[78] The tetraketone yields with zinc and acetic acid a dihydro-derivative (XXXVII) which closely resembles dihydrorhodoxanthin (p. 156) in its enolic properties. Like β-carotene, but

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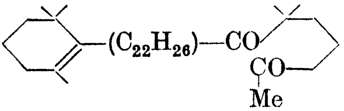
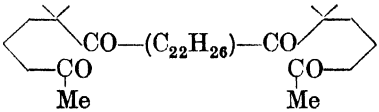
[76] R. Kuhn and A. Winterstein, *Ber.*, 1933, **66**, [*B*], 429; *A.*, 387. The course of oxidation in polyenes depends on the number of double bonds, the length of chain, and other not yet understood circumstances, and the quantitative evidence afforded in the case of β-carotene is insufficiently significant to preclude the possibility that the molecule has similar ends.

[77] R. Kuhn and H. Brockmann, *Ber.*, 1933, **66**, [*B*], 1319; *A.*, 1297.

[78] *Idem, ibid.*, 1932, **65**, [*B*], 894; *A.*, 1932, 749; *Z. physiol. Chem.*, 1932, **213**, 1; *A.*, 1933, 195. The preferential attack of oxidising agents at the terminal double bonds of the carotene system is a remarkable feature.

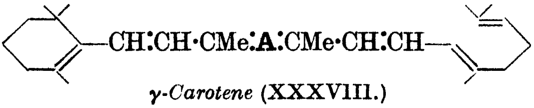

Semi-β-carotinone (XXXV.)


β-Carotinone (XXXVI.)

$$Me{\cdot}CO{\cdot}[CH_2]_3{\cdot}CMe_2{\cdot}CO{\cdot}CH_2{\cdot}CH{:}CMe\text{–}\mathbf{B}\text{–}CMe{:}CH{\cdot}CH_2{\cdot}CO{\cdot}CMe_2{\cdot}[CH_2]_3{\cdot}COMe$$
(XXXVII.)

unlike β-carotinone, semi-β-carotinone shows strong growth-promoting action, as might be expected if, as R. Kuhn and H. Brockmann believe, 1 mol. of β-carotene is the precursor of 2 mols. of vitamin A in the animal body; [79] for, if only one ring system of β-carotene suffers fission, 1 mol. of vitamin A should still be capable of arising ($C_{40}H_{56} + 2H_2O \longrightarrow 2C_{20}H_{30}O$). In this connexion it may be mentioned that a β-carotene monoxide,[80] prepared by the action of perbenzoic acid on β-carotene, and a hydroxy-β-carotene ($C_{40}H_{58}O_3$), obtained by the action of chromic acid on β-carotene,[78] both promote growth, and there is little doubt that in the formation of both derivatives only one ring system has been attacked.

γ-Carotene, m. p. 178° (corr.), which appears to constitute about one thousandth part of ordinary carotene,[81] is successfully separated from the α- and the β-form by adsorption on aluminium oxide. Like β-carotene, it is optically inactive, but it differs from both the other forms in taking up, not eleven, but twelve molecules of hydrogen and in yielding on degradation only 0·85 mol. of acetone. In various properties (especially the position of its absorption bands) it takes a position between β-carotene and lycopene and its structure is best represented by (XXXVIII), that is, as containing one of the opened-ionone rings characteristic of lycopene.


γ-Carotene (XXXVIII.)

γ-Carotene strongly promotes growth to an extent nearly equal to that of α- or β-carotene. Thus in hydrocarbons of the composition $C_{40}H_{56}$ such biological activity appears not to be dependent on the number of double bonds, which may be 10, 11, or 12, or necessarily to be lost when the molecule is modified; [78] an essential feature, however, according to R. Kuhn and H. Brockmann, appears to be the presence of at least one carbon ring of β-ionone type, but other special conditions may possibly need fulfilling.

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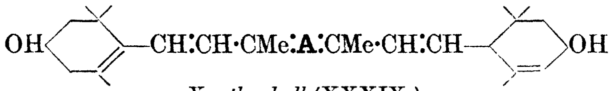
[79] R. Kuhn and H. Brockmann, *Klin. Woch.*, 1933, **12**, 972; *A.*, 1212.

[80] H. v. Euler, P. Karrer, and O. Walker, *Helv. Chim. Acta*, 1932, **15**, 1507.

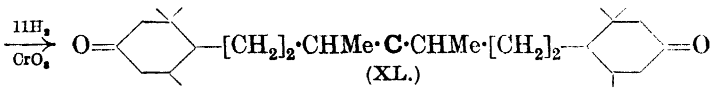
[81] R. Kuhn and H. Brockmann, *Ber.*, 1933, **66**, [*B*], 407; *A.*, 431. The average composition of investigated carotene preparations is: α-, 15%; β-, 85%; and γ-, 0·1%.

Xanthophyll or Phytoxanthin Group (*Lutein, Violaxanthin, Zeaxanthin, Physalien, Taraxanthin, Fucoxanthin, Capsanthin, Flavoxanthin, Kryptoxanthin*).—For the C_{40}-carotenoids which contain oxygen, P. Karrer and A. Notthafft propose the generic term "phytoxanthins," whilst they reserve the name "xanthophyll" for the substance $C_{40}H_{56}O_2$ derived from green leaves;[82] this substance, however, is designated "lutein" by R. Kuhn, A. Winterstein, and E. Lederer.[83] The substances of the group, so far as is determined, contain hydroxylated ionone rings, and frequently in the plant the hydroxyl groups are esterified by fatty acids.

To lutein or leaf-xanthophyll, which not only occurs in the green leaves and yellow petals of various plants but constitutes one of the colouring matters of egg-yolk, P. Karrer and A. Zubrys[84] have assigned the formula (XXXIX), thus representing it to be a dihydroxy-derivative of α-carotene. Since its perhydro-derivative yields a diketone (presumably XL) on oxidation with chromic acid, there is no doubt that the hydroxyl groups are of secondary type.



Xanthophyll (XXXIX.)



(XL.)

Violaxanthin, which occurs in pansy, laburnum, nettles, and horse chestnut leaves, is an allied substance containing four oxygen atoms, of which three appear to be present as hydroxyl groups. The constitutions of other known compounds of the xanthophyll group, *viz.*, fucoxanthin ($C_{40}H_{56}O_6$), flavoxanthin ($C_{40}H_{56}O_3$), capsanthin ($C_{35}H_{50}O_3$), and taraxanthin ($C_{40}H_{56}O_3$), have not yet been determined.

Zeaxanthin accompanies lutein in egg-yolk and occurs with rhodoxanthin in the ripe fruits of yew (*Taxus baccata*). It has recently been formulated as a dihydroxy-β-carotene (XLI).[85] In the red calyces and berries of the *Physalis* species it occurs as its dipalmitate, to which the name physalien was originally given.

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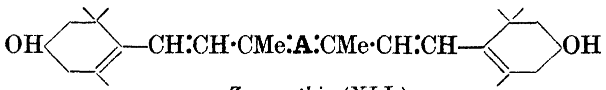
[82] *Helv. Chim. Acta*, 1932, **15**, 1195; *A.*, 1932, 1256.

[83] *Z. physiol. Chem.*, 1931, **197**, 141; *A.*, 1931, 885.

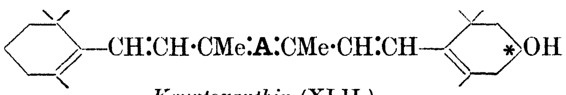
[84] *Helv. Chim. Acta*, 1933, **16**, 977; *A.*, 1150.

[85] R. Kuhn and H. Brockmann, *Ber.*, 1933, **66**, [*B*], 828; *A.*, 716.



Zeaxanthin (XLI.)

Flavoxanthin, $C_{40}H_{56}O_3$, isolated from *Ranunculus acer*,[86] was the first xanthophyll found to contain an odd number of oxygen atoms. A second pigment of the same type, kryptoxanthin, $C_{40}H_{56}O$, occurs in esterified condition as a main constituent of the dye in the red calyces and berries of the *Physalis* species from which physalien was originally isolated. Previously it had not been differentiated therein from β-carotene, which it closely resembles and accompanies; now, however, it has been isolated by chromatographic analysis, but cannot be distinguished from β-carotene spectroscopically. It contains a hydroxyl group and, since it takes up 11 mols. of hydrogen, without doubt contains two carbon rings. In colour, tendency to become adsorbed, and yield of acetic acid on complete oxidation with chromic acid it occupies a position between β-carotene and zeaxanthin; accordingly R. Kuhn and C. Grundmann suggest a formula (XLII) comprising half the β-carotene and half the zeaxanthin molecule.[87] In optical activity, however, there appears to be an anomalous relationship between kryptoxanthin on the one hand and β-carotene (inactive) and zeaxanthin (lævorotatory) on the other, for any rotation which is observable is extremely small. According to formula (XLII) kryptoxanthin contains one (unmodified) β-carotene residue and according to Kuhn and Brockmann's views should therefore show half the vitamin-A activity of β-carotene and differ from zeaxanthin, which has no such residue. Actually, kryptoxanthin adds to the existing list of naturally occurring pro-vitamins (α-, β- and γ-carotene) a fourth example.



Kryptoxanthin (XLII.)

Azafrin.—Azafrin, which gives rise to many magnificent colour reactions, especially with mineral acids, is extracted from azafran root.[88] It has been shown to be a carotenoid carboxylic acid containing seven conjugated double bonds and four oxygen atoms—the latter probably tertiary. The C_{28}-formula first suggested represented the nearest methyl group to the carboxyl group as attached to the δ-carbon atom. But since azafrin yields *m*-xylene, *m*-toluic acid, and toluene on thermal degradation, this methyl group must be attached either to the γ- or to the ε-carbon atom. The C_{28}-formula has now been replaced by a C_{27}-formula ($C_{27}H_{52}O_4$) (XLIII) which agrees more closely with new analytical results and permits the representation of the azafrin molecule as derived from carotene by the loss of thirteen carbon atoms (*i.e.*, one complete ionone skeleton); the first methyl group then occurs in the γ-position.[89]

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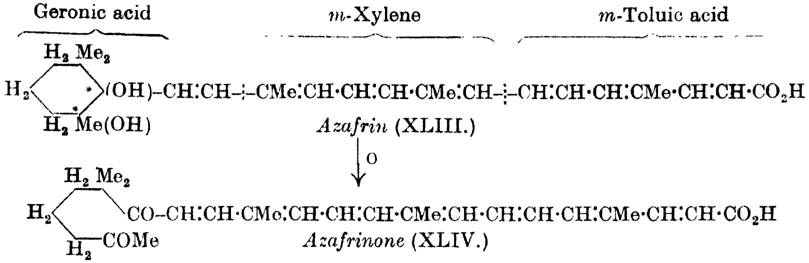
[86] R. Kuhn and H. Brockmann, *Z. physiol. Chem.*, 1932, **213**, 192; *A.*, 1933, 329.

[87] *Ber.*, 1933, **66**, [*B*], 1746.

[88] R. Kuhn, A. Winterstein, and H. Roth, *Ber.*, 1931, **64**, [*B*], 333; *A.*, 1931, 492.



Azafrin (XLIII.)

Azafrinone (XLIV.)

By careful oxidation of azafrin, azafrinone (XLIV) is produced, which takes up seven molecules of hydrogen easily and two more with difficulty; but in this oxidation the optical activity characteristic of azafrin is lost and its original presence must be attributed to the asymmetry of an adjacent pair of carbon atoms (* * in XLIII) in the carbon ring. Azafrin which has been reduced to the point of saturation of its seven ethylenic bonds yields on oxidation with lead tetra-acetate a compound identical with reduced (tetradecahydro-)azafrinone; moreover, azafrin yields with permanganate geronic acid. Thus it is evident that the hydroxyl groups of azafrin are differently placed from those which form the characteristic feature of the xanthophyll group; indeed azafrin is a di-tertiary glycol in which the hydroxyl groups probably occupy *trans*-positions. The methyl ester of azafrin, like that of various conjugated di-esters and di-ketones (not mono-), is capable of smooth reduction by zinc and acetic acid to the dihydro-stage; and like the dihydro-derivatives of crocetin, bixin, rhodoxanthin, etc., the sodium or potassium derivative is intensely coloured and reverts to the parent polyene by the action of air.

Rhodoxanthin.—The red fruits of the yew (*Taxus baccata*) yield a very stable blue-black crystalline pigment, $C_{40}H_{50}O_2$. The poverty in hydrogen shown by this formula agrees with the presence of an exceptionally large number of double bonds in the azafrin molecule—a characteristic reflected in the especially long-wave position of the absorption bands. The pigment contains no esterifiable hydroxyl groups, but yields a dioxime; moreover, spectrographic evidence indicates that the oxime-forming carbonyl groups are conjugated with the unsaturated chain of the molecule and chemical evidence shows that rhodoxanthin represents a new type of polyene pigment, *viz.*, a polyene ketone.[90]

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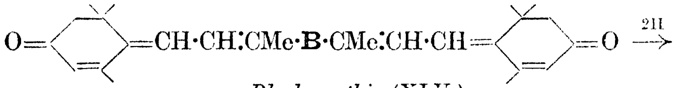
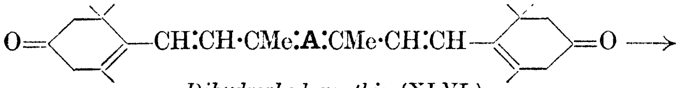
[89] R. Kuhn and A. Deutsch, *Ber.*, 1933, **66**, [*B*], 883; *A.*, 711.

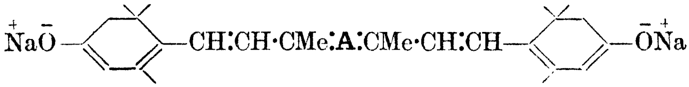
Rhodoxanthin is the most unsaturated of the known carotenoids and takes up easily twelve molecules of hydrogen and with greater difficulty a further two molecules. This behaviour corresponds to the saturation of twelve ethylenic linkages, followed by the reduction of two carbonyl groups; and since the saturated diketone produced in the first of these stages has the composition $C_{40}H_{74}O_2$ and the saturated diol finally produced has the composition $C_{40}H_{78}O_2$, two carbon rings must be present as represented in (XLV).



Rhodoxanthin (XLV.)



Dihydrorhodoxanthin (XLVI.)



Disodiodihydrorhodoxanthin (XLVII.)

The passage from rhodoxanthin to its dihydro-derivative (XLVI) is marked by a lightening in colour as in the case of bixin and crocetin. Spectroscopically the dihydro-compound resembles β-carotene and zeaxanthin to the point of confusion; and since the dihydro-compound and its dioxime agree with one another spectroscopically, it can be deduced that the addition of two hydrogen atoms has interrupted the conjugation of the carbonyl groups with the polyene chain. Like dihydrocrocetin dimethyl ester, methyldihydrobixin,[91] and the above-mentioned dihydro-β-carotenone, dihydrorhodoxanthin gives with alcoholic soda an intensely coloured sodio-derivative (XLVII), which reverts by the action of air to the parent polyene.

Vitamin A.—Certain naturally occurring polyene pigments, especially β-carotene, are capable of promoting growth in animals, thus acting as sources of vitamin A. Those carotenoids which contain one or two unmodified β-ionone rings appear to suffer degradation in the animal organism to vitamin A (see p. 152). Vitamin A itself is found in the liver and blood serum of animals and is reported to occur in butter;[92] the richest concentrations, however, are found in the livers of sea-fish, but there is an enormous difference in the vitamin A potency of the liver oils from different species and also in that of different specimens of oil from a single species.[93]

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[90] R. Kuhn and H. Brockmann, *Ber.*, 1933, **66**, [*B*], 828; *A.*, 716.

[91] *Ann. Reports*, 1932, **29**, 121.

P. Karrer and his collaborators have found[94] that the liver oil of *Hippoglossus hippoglossus*, a variety of halibut rich in vitamins,[95] is a suitable material for obtaining highly active preparations of vitamin A. Such preparations can be distilled in part at reduced pressure without decomposition, and, since they yield geronic acid on ozonolysis, contain, like β-carotene, the β-ionone residue; furthermore the yield of geronic acid increases with the Lovibond figure for the amount of vitamin A present. The molecular weight of vitamin A, determined by the Rast method, is about 320, and from the nature of the colour reactions and the extent to which the preparations (*a*) yield acetic acid (from the $\dot{\mathrm{C}}\mathrm{H{\cdot}CMe}\dot{}$ groups) on oxidation and (*b*) undergo catalytic hydrogenation, it is deduced that vitamin A has a polyene constitution analogous to that of carotene.

Experiments with a still more active preparation from the liver-oil of a variety of mackerel (*Scombresox saurus*) revealed that the vitamin is an alcohol, capable of esterification, which after purification by fractional adsorption on alumina has the formula $C_{20}H_{30}O$ or, less probably, $C_{22}H_{32}O$.[96] Vitamin A obtained from both *Scombresox* and *Hippoglossus* was a pale yellow viscous oil which probably contained a small proportion of related substances but nothing of entirely foreign nature, nor any considerable proportion of sterols or vitamin D. From considerations relating to (*a*) the yield of geronic acid[97] and acetic acid obtained by oxidation of the

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[92] R. A. Morton and I. M. Heilbron, *Biochem. J.*, 1930, **24**, 870; *A.*, 1321.

[93] For details regarding the methods of determination and the spectrographic criteria of vitamin A, see J. C. Drummond and R. A. Morton, *ibid.*, 1929, **23**, 785; *A.*, 1929, 1202; R. A. Morton, I. M. Heilbron, and F. S. Spring, *ibid.*, 1930, **24**, 136; *A.*, 1930, 380; A. Chevallier and P. Chabre, *ibid.*, 1933, **27**, 298; *A.*, 540.

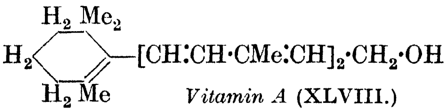
[94] P. Karrer and H. v. Euler, *Naturwiss.*, 1931, **19**, 676; *A.*, 1931, 1195; P. Karrer, H. Morf, and K. Schöpp, *Helv. Chim. Acta*, 1931, **14**, 1036, 1040; *A.*, 1931, 1463.

[95] E. Poulson, *Strahlenther.*, 1929, **34**, 648; *A.*, 1930, 1070; S. Schmidt-Nielssen, *Biochem. J.*, 1929, **23**, 1153; *A.*, 1930, 255.

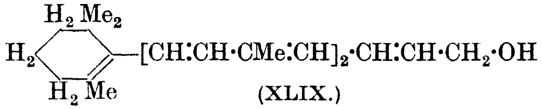
[96] P. Karrer, R. Morf, and K. Schöpp, *loc. cit.*; P. Karrer, O. Walker, K. Schöpp, and R. Morf, *Nature*, 1933, **132**, 26; *A.*, 805.

[97] On the basis of the yields of geronic acid obtained in analogous decompositions, the preparation is calculated to have contained 50—80% of vitamin A.

Scombresox preparation, (*b*) the molecular weight (300—320), (*c*) the amount of hydrogen absorbed catalytically, and (*d*) the composition of the reduction product, the C_{20}-formula (XLVIII) was tentatively assigned to vitamin A by P. Karrer, R. Morf, and K. Schöpp, but the C_{22}-formula (XLIX) was not entirely excluded.



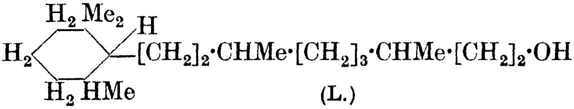
Vitamin A (XLVIII.)



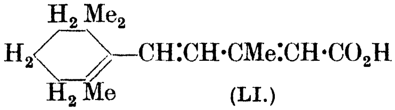
(XLIX.)

According to (XLVIII), vitamin A represents exactly half the β-carotene molecule with the terminal carbon atom combined with the elements of water.

Karrer and Morf subsequently synthesised a compound, described as " perhydro-vitamin-A " (L), by reducing the easily obtained triene-acid (LI) and extending the carbon chain of the reduced acid by a series of simple operations. This compound is reported to be identical with fully hydrogenated natural vitamin A.



(L.)



(LI.)

I. M. Heilbron, R. A. Morton, J. C. Drummond, and their collaborators[98] have purified vitamin A concentrates from halibut liver-oil at a pressure below 0·00001 mm.: at this pressure the vitamin distils without decomposition at 137—138° as a pale yellow viscous oil of approximately the composition $C_{20}H_{30}O$, and of molecular weight 320 ± 15; there is little spectrographic difference between samples so purified and those purified by the chromatographic method. The same authors have carried out an exhaustive spectrographic examination of vitamin A preparations from various mammalian and fish-liver oils with the object of arriving at a conclusion respecting the homogeneity of the vitamin product. The absorption spectra do not afford entirely conclusive evidence of homogeneity, and although observations are impressively in favour of the structural representation (XLVIII) for vitamin A, they are not as yet conclusively so; moreover, from the standpoint of analytical data, the failure to prepare crystalline derivatives of vitamin A and the indication over a very large number of ultimate analyses of some slight degree of variability from the $C_{20}H_{30}O$ formula, render any claim to have isolated vitamin A in a state of purity at the present stage somewhat insecure.

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[98] *Biochem. J.*, 1932, **26**, 1178; *A.*, 1932, 1174.

Partial confirmation of Karrer's formulation of vitamin A has been obtained by degradation. A vitamin A concentrate, when dehydrogenated with selenium at 300—330°, gave a good yield of 1 : 6-dimethylnaphthalene, thus showing that the concentrate contained a substance whose constitution as far as the fourteenth carbon atom must be identical with that shown in (XLVIII).[99]

Natural Flavin Dyes (Lyochromes).

A number of naturally occurring colouring matters which appear to belong to the same group of water-soluble nitrogenous dyes have been isolated from different sources and by different workers. P. Ellinger and W. Koschara have isolated from whey three crystalline dyes of red or reddish-yellow colour which are rich in nitrogen and oxygen and show strong yellow-green fluorescence in aqueous solution.[1] They suggest that these three dyes are related to two oxidation-ferments, obtained by O. Warburg and W. Christian,[2] and to others contained in urine. R. Kuhn and his collaborators have independently described two dyes of nitrogenous water-soluble type.[3a] One of these, constituting the colouring matter of egg-albumen, displays in solution strong green fluorescence; the other, isolated from whey, appears to be different from Ellinger and Koschara's preparation and displays strong green fluorescence. The name " flavins " is suggested for the new group.

The dye from white-of-egg (180 mg. from about 10,000 eggs), which has been termed " ovoflavin," [3b] can be extracted by alcohols and purified by adsorption on fuller's earth; it has approximately the composition $C_8H_{10}O_3N_2$, but the double formula $C_{16}H_{20}O_6N_4$ or even $C_{17}H_{20}O_6N_4$ may be correct. It resembles spectroscopically a dye, $C_{12}H_{12}O_2N_4$, obtained by Warburg and Christian from yeast,[4] and is very stable towards mineral acids and oxidising agents but is decomposed by alkalis. It is reduced (decolorised) by reducing agents and regains its colour on shaking with air, the change, flavin $\rightleftharpoons$ leucoflavin, depending on oxygen transference.

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[99] I. M. Heilbron, R. A. Morton, and E. T. Webster, *Biochem. J.*, 1932, **26**, 1194; *A.*, 1932, 1174.

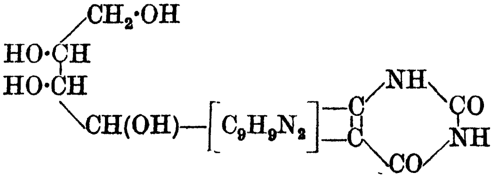
[1] P. Ellinger and W. Koschara, *Ber.*, 1933, **66**, [*B*], 315, 808; *A.*, 298, 847. Compare B. Bleyer and O. Kallmann, *Biochem. Z.*, 1925, **155**, 54; *A.*, 1925, i, 457. Ellinger and Koschara originally proposed the name " lyochromes " for dyes of the new type.

[2] *Biochem. Z.*, 1932, **254**, 438; *A.*, 1932, 1285.

[3] R. Kuhn, P. György, and T. Wagner-Jauregg, *Ber.*, 1933, **66**, [*B*], (*a*) p. 317, (*b*) p. 576, (*c*) p. 1034; *A.*, 298, 522, 847.

The dyes of this new group offer a strong contrast in composition, solubility, fluorescence, sensitivity towards acids, alkalis, and oxidising agents, and in biological activity to the carotenes (lipochromes). The crystalline orange-brown dye from whey, termed lactoflavin [3c] (nearly 1 g. from 5,400 litres of whey), was obtained by Kuhn and his collaborators in their attempts to concentrate the vitamin B_2 from this source. It has the composition $C_{17}H_{20}O_6N_4$ and resembles ovoflavin closely in decomposition point and in absorption spectrum. Both ovoflavin and lactoflavin appear to be related to vitamin B_2, and Kuhn and his co-workers state that the crystalline lactoflavin not only represents the most active preparation of vitamin B_2 yet obtained, but is probably identical therewith.[5] Lactoflavin yields with sodium bisulphite, sodium hydrosulphide, zinc dust and acid, or hydrogen and platinum, a leuco-derivative which (*a*) reverts to the original dye or (*b*) passes by successive illumination, oxidation, and treatment with cold alkali through two well-defined intermediate stages into a crystalline compound, $C_{13}H_{12}O_2N_4$ (lumilactoflavin). The latter when boiled with alkali suffers loss of urea and yields a crystalline compound, $C_{12}H_{12}O_3N_2$, which is in turn decomposed by heat into carbon dioxide and a crystalline substance, $C_{11}H_{12}ON_2$. From a consideration of these changes the partial formulation (LII) is tentatively put forward.

(LII.)



Peroxides and Oxidation Processes.

Aldehydes and ketones yield peroxides which hitherto have been known only in multimolecular form. They are similarly constituted to cyclic polymeric aldehydes, except that the oxygen atoms of the latter are wholly or partly replaced by the peroxide group; the simplest example of such alkylidene peroxides is ethylidene peroxide (LIII). Simple and multimolecular ozonides represent mixed peroxidic compounds of a related type: indeed unimolecular (as also multimolecular) ethylene ozonide (LIV) belongs to a class of cyclic acetals of which A. Rieche and R. Meister[6] have now obtained a definite example in mono-perparaldehyde. In the formation of this substance, water is split off from bishydroxyethyl peroxide (LV) (2 mols.), a cyclic peroxide (LVI) thus being produced which in constitution is a dimeric ozonide. This " synthetic dimeric ozonide " has in fact properties intermediate between those of true uni- and multi-molecular butylene ozonide and indeed it represents an intermediate stage between the two, but is not so stable as either. There arises, however, in addition, monomeric butylene ozonide, which is identical with that obtainable by ozonising butylene. The dimeric ozonide appears to break down to ethylidene peroxide when kept in a vacuum, but yields on cautious distillation mono-perparacetaldehyde (LVII). The latter compound is a peroxidic analogue of paraldehyde and its formation is probably due to a cracking process in which ethylidene peroxide is split off.

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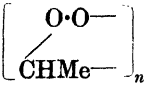
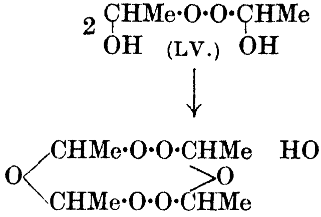
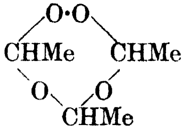
[4] *Naturwiss.*, 1932, **20**, 688; *A.*, 1932, 1164; *Biochem. Z.*, 1933, **257**, 492; *A.*, 424.

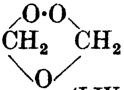
[5] R. Kuhn, H. Rudy, and T. Wagner-Jauregg, *Ber.*, 1933, **66**, [*B*], 1950.


(LIII.)


(LV.)

(LVI.)

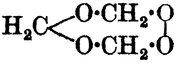

(LVII.)

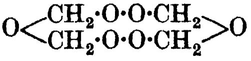

(LIV.)

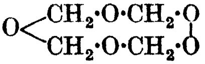
$HO{\cdot}CH_2{\cdot}O{\cdot}O{\cdot}CH_2{\cdot}OH$ (LVIII.)

$HO{\cdot}CH_2{\cdot}O{\cdot}OR$ (LIX.)

The peroxides of the formaldehyde series hitherto known are bishydroxymethyl peroxide (LVIII) and hydroxymethyl alkyl peroxides (LIX), obtained by adding formaldehyde to hydrogen peroxide and to alkyl hydrogen peroxide respectively.[7] The former of these peroxides reacts with two further molecules of formaldehyde to give the bishydroxymethyl derivative, $(OH{\cdot}CH_2{\cdot}O{\cdot}CH_2{\cdot}O{\cdot})_2$, which by prolonged action of phosphoric oxide yields pertrioxymethylene (LX), or by more intense action of the same reagent, tetraoxymethylene diperoxide (LXI).[8] Both of these cyclic


(LX.)


(LXI.)


(LXII.)

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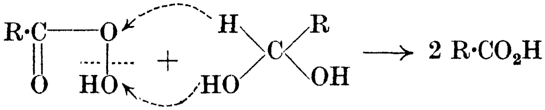
[6] *Ber.*, 1932, **65**, [*B*], 1274; *A.*, 1932, 1114.

[7] *Ann. Reports*, 1931, **28**, 85.

[8] A. Rieche and R. Meister, *Ber.*, 1933, **66**, [*B*], 718; *A.*, 592; A. Rieche, *Angew. Chem.*, 1932, **45**, 441; *A.*, 1932, 831.

peroxides are explosive, the pertrioxymethylene yielding on explosion trioxymethylene and a compound which is possibly pertetraoxymethylene (LXII).

Acetaldehyde with oxygen or air rapidly gives a substance which in water has the properties of a per-acid.[9] According to H. Wieland and D. Richter [10] the reaction between aldehydes and molecular oxygen consists in the first stage, under all observed conditions, in the primary formation of a per-acid : the two reactants directly unite and it is the true aldehyde form (not the hydrate) which suffers autoxidation. The final stage in the autoxidation consists in interchange between per-acid and aldehyde, yielding acid ($\cdot CO_3H + \cdot CHO \longrightarrow 2\ \cdot CO_2H$), but the course of this reaction remains uncertain. Since peracetic acid and acetaldehyde do not react in the dry state, the reaction occurring between them in presence of water probably does so because the per-acid acts as hydrogen acceptor towards the hydrated aldehyde :



The slow oxidation of the aldehyde which takes place in a mixture of dry perbenzoic acid and dry acetaldehyde is, however, probably due to the decomposition of an additive compound

$$(BzO{\cdot}O{\cdot}CHMe{\cdot}OH \longrightarrow BzOH + Ac{\cdot}OH),$$

but in general the aldehyde hydrate appears to be responsible for the rapid oxidation of aldehydes in presence of water. In the slow oxidation of acetaldehyde with ammonium persulphate, the ·O·O· bridge probably acts as hydrogen acceptor.

The unsatisfactory results frequently obtained in the oxidation of aldehydes to acids by hydrogen peroxide and alkali are attributed by J. von Braun and W. Keller [11] to the slowness of the changes involved in (*a*) the formation of a primary additive product OH·CHR·O·OH or OH·CHR·O·O·CHR·OH, (*b*) its conversion by loss of water, or dissociation, into $R{\cdot}CH{<}\begin{matrix}O\\|\\O\end{matrix}$, and (*c*) the final transformation into $R{\cdot}CO_2H$, as a result of which opportunity is afforded for the excess of hydrogen peroxide to attack any incompletely stable radical R. Oxidation with molecular oxygen is too slow for preparative purposes and is not greatly accelerated by ferrous iron : finely divided manganese dioxide (even 1/4000 mol.), however, or, preferably, potassium permanganate is a suitable accelerator which retains its activity over long periods. The manganese catalyst probably owes its activity to its interaction with the carbonyl group, whereby an unstable additive compound is produced which renders the aldehyde more sensitive to oxygen; but when an olefin is added to the reaction mixture, the oxidation of the aldehyde is retarded, because the olefin is then more favoured by the catalyst than is the aldehyde. Oxidation of acetaldehyde by acidified hydrogen peroxide at 95° yields largely methane and hydrogen, and that of propaldehyde largely ethane and hydrogen.[12] The mechanism for such reactions proposed by H. Wieland [13] is disputed.

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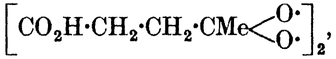
[9] W. H. Hatcher, E. W. R. Steacie, and F. Howland, *Canadian J. Res.*, 1931, **5**, 648; *A.*, 1932, 253.

[10] *Annalen*, 1932, **495**, 284; *A.*, 1932, 722.

[11] *Ber.*, 1933, **66**, [*B*], 215; *A.*, 259.

F. Fichter and S. Lurie [14] have now obtained synthetically, by the action of hydrogen peroxide on ethyl lævulate, the ester of the same bimolecular ketoperoxide,  $\left[CO_2H{\cdot}CH_2{\cdot}CH_2{\cdot}CMe{<}\begin{matrix}O\cdot\\O\cdot\end{matrix}\right]_2$, as was first isolated by C. Harries from the ozonolysis products of rubber and later formulated by R. Pummerer and his collaborators.[15] A higher homologue of this compound derived from ε-keto-*n*-octoic acid has also been obtained.[16] Fichter and Lurie have tried by various methods to prepare a true carbonyl peroxide containing the group ·CO·O·O·CO·, but without success.[16, 17] Whether such peroxides are formed at any stage during the action of hydrogen peroxide on acids, by the electrolysis of the salts of monobasic acids, or by the oxidising action of potassium persulphate on the salts of acids, is uncertain, but at all events they do not survive.

S. S. Medvedev and E. N. Alexeeva have endeavoured to apply the original method of Baeyer and Villiger to the preparation of the higher alkyl peroxides and have obtained by the action of hydrogen peroxide and alkali on di*iso*propyl sulphate, *iso*propyl hydrogen peroxide.[18] This compound yields the salt

$$Pr^{\beta}O{\cdot}O{\cdot}Ba{\cdot}O{\cdot}O{\cdot}Pr^{\beta},3H_2O,$$

which is convertible by terephthalyl chloride into the peroxidic ester $C_6H_4(CO{\cdot}O{\cdot}OPr^{\beta})_2$. Attempts to prepare peroxidic compounds of the camphoric acid series have been successful, and percamphoric acid has been applied to the determination of unsaturation.[19]

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[12] S. Bezzi, *Gazzetta*, 1933, **63**, 345; *A.*, 1036.

[13] *Ber.*, 1921, **54**, 2353; *A.*, 1921, i, 889.

[14] *Helv. Chim. Acta*, 1931, **14**, 1445; *A.*, 1932, 43.

[15] *Ann. Reports*, 1931, **28**, 85.

[16] *Helv. Chim. Acta*, 1933, **16**, 885; *A.*, 807.

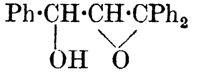
[17] F. Fichter and L. Panizzon, *ibid.*, 1932, **15**, 996; *A.*, 1932, 929.

[18] *Ber.*, 1932, **65**, [*B*], 131; *A.*, 1932, 363.

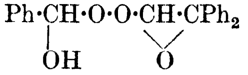
[19] N. A. Milas and A. McAlevy, *J. Amer. Chem. Soc.*, 1933, **55**, 349; *A.*, 279; N. A. Milas and I. S. Cliff, *ibid.*, p. 352; *A.*, 279.

Much interest has been shown in the nature and mechanism of autoxidation processes. A remarkable example is afforded by the autoxidation of the oxido-triphenylpropyl alcohol (LXIII) to the peroxide (LXIV).[20] This reaction proceeds in air which contains a little hydrogen chloride (not in acid-free air) and appears to involve first cleavage to benzaldehyde and diphenylethylene oxide, then autoxidation of the benzaldehyde, and finally synthesis of

(LXIII.)



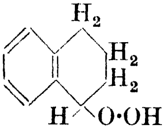
$$\mathrm{Ph{\cdot}\underset{OH}{\underset{|}{CH}}{\cdot}\underset{\diagdown O \diagup}{CH{\cdot}CPh_2}}$$



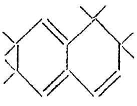
$$\mathrm{Ph{\cdot}\underset{OH}{\underset{|}{CH}}{\cdot}O{\cdot}O{\cdot}\underset{\diagdown O \diagup}{CH{\cdot}CPh_2}}$$

(LXIV.)

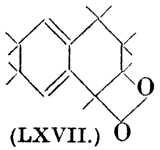
the peroxide from the diphenylethylene and the autoxidation product of benzaldehyde. Another interesting example is that of tetrahydronaphthalene, which by the prolonged passage of air at 75° yields a peroxide, apparently of formula (LXV): it is suggested that the peroxide is derived from a tetrahydronaphthalene of the form (LXVI) *via* the form (LXVII).[21]



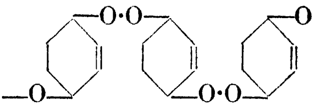
(LXV.)



(LXVI.)



(LXVII.)



(LXVIII.)

According to K. Bodendorf,[22] conjugated cyclic dienes are oxidised by oxygen without a catalyst much more rapidly than are mono-ethylenic compounds, and the products are multimolecular peroxides of type (LXVIII). The reaction is autocatalytic, but the catalytically active substance ("inductor") formed during the reaction is unstable. Thus, a small amount of freshly oxidised α-terpinene very greatly increases the rate of oxidation of a second batch, but the isolated peroxide, or oxidised material which has been kept for some time, is inactive. Similarly, interruption of the oxidation leads to decreased velocity when oxidation is resumed, the decrease being the greater the longer is the interruption. The inductor from α-phellandrene catalyses the oxidation of α-phellandrene, but not that of α-terpinene, whereas the inductor from α-terpinene catalyses the oxidation of both α-terpinene and α-phellandrene. The last is regarded as an example of true induced oxidation, which probably plays an important part in biological reactions. The inductor is assumed to be a moloxide. α-Terpinene and α-phellandrene both yield undistillable (multimolecular) peroxides.

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[20] E. P. Kohler and E. M. Nygaard, *J. Amer. Chem. Soc.*, 1933, **55**, **310**; *A.*, 271.

[21] H. Hock and W. Susemihl, *Ber.*, 1933, **66**, [*B*], 61; *A.*, 153.

[22] *Arch. Pharm.*, 1933, **271**, 1; *A.*, 279.

The autoxidation of linoleic acid is catalysed by numerous basic compounds, by dihydroxyacetone and related compounds, by carotene and related compounds (not bixin), by metal salts, and by various other materials; the autoxidation of oleic acid is similarly catalysed by various basic compounds, but the autoxidation of both substances may be inhibited by the addition of certain other compounds.[23] Ferrous iron catalyses the autoxidation of phenols with the production of black humus-like products, but this only applies when the hydroxyl groups are not replaced by alkyl groups.[24] The autoxidation process is not accelerated by ferrous iron unless the conditions necessary for the formation of hydrogen peroxide are fulfilled, and the hypothesis is put forward that the catalytic influence of the iron is exercised in promoting the action of initially formed hydrogen peroxide. The autoxidation of methyldihydrobixin proceeds in the presence of amines to the absorption of ten atoms of oxygen per molecule without coming to a definite end; with caustic soda, rapid absorption of two atoms of oxygen takes place, followed by a much slower consumption of oxygen.[25] The carotenoids, including vitamin A, themselves act as catalysts[26] in promoting the autoxidation of fatty acids but not of glycerides, and in the presence of hæmin they promote a considerable degree of autoxidation of neutral unsaturated oils; when, however, they are employed with other substances, other effects are observed. Studies of the mechanism of autoxidation of α-ketols have been made by A. Weissberger,[27] and of the autoxidation products of piperitone by W. Treibs.[28]

The existing evidence that peroxides and ozonides are effective catalysts for polymerisation of both hydrocarbons and aldehydes is strengthened by the experiments of J. B. Conant and W. R. Peterson[29] on the polymerisation of aliphatic aldehydes and isoprene under high pressures (12000 atm.). Here peroxide catalysis is essential to polymerisation (very minute proportions of catalyst are sufficient) and the effect of the increased pressure is only to accelerate the reaction. The rate of polymerisation of *n*-butaldehyde parallels the amount of oxygen which has been absorbed before the pressure treatment commences; and whatever the nature of the actual catalyst may be it is considered not to be an intermediate between the aldehyde and the acid formed therefrom. Polymerisations of this kind can be catalysed by added peroxides (*e.g.*, benzoyl peroxide) or greatly hindered by anti-oxidants such as hexaphenylethane and it is supposed that they result from a series of chain reactions initiated in the liquid by the spontaneous decomposition from time to time of the single molecules of peroxidic catalyst. The accelerating effect of great pressure is accordingly due to the orienting of the molecules of aldehyde or isoprene into more compact bundles in which longer reaction chains can be propagated by the decomposing catalyst. The accelerating effect of temperature is attributed to the more frequent peroxide decompositions which occur when the temperature rises, and the efficiency of a given peroxide as catalyst depends on its instability. The polymeric aldehydes formed by these polymerisation processes cannot be stabilised.

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[23] W. Franke, *Annalen*, 1932, **498**, 129; *A.*, 1932, 1112; P. Rona, R. Asmus, and H. Steineck, *Biochem. Z.*, 1932, **250**, 149; *A.*, 1932, 1003.

[24] A. Bach, *Ber.*, 1932, **65**, [*B*], 1788; *A.*, 1933, 155.

[25] R. Kuhn, P. J. Drumm, M. Hoffer, and E. F. Möller, *Ber.*, 1932, **65**, [*B*], 1785; *A.*, 1933, 52.

[26] W. Franke, *Z. physiol. Chem.*, 1932, **212**, 234; *A.*, 1933, 49.

[27] *Ber.*, 1932, **65**, [*B*], 1815; *A.*, 1933, 161; see also A. Weissberger, H. Mainz, and E. Strasser, *ibid.*, 1929, **62**, [*B*], 1942; *A.*, 1929, 1301.

[28] *Ibid.*, 1930, **63**, [*B*], 2423; *A.*, 1931, 94; *ibid.*, 1931, **64**, [*B*], 2178; *A.*, 1931, 1299; *et seq.*

[29] *J. Amer. Chem. Soc.*, 1932, **54**, 628; *A.*, 1932, 367; see also J. B. Conant and C. O. Tongberg, *ibid.*, 1930, **52**, 1659; *A.*, 1930, 735.

An important catalytic effect of peroxides has recently been observed in additive reactions:[30] traces of peroxidic material present as impurities in allyl bromide, vinyl bromide, and propylene (or even small quantities of added peroxides) reverse the normal direction of addition of hydrogen bromide to these substances.

A number of new oxidising agents have been brought into use for specific purposes. Lead tetra-acetate has been successfully employed by R. Criegee[31] and subsequent workers for the oxidation of ethylenic substances and the oxidative fission of α-glycols; periodic acid has been applied to the oxidation of hydroxy-acids, sugars, polyhydric alcohols, and α- and β-glycerophosphoric acids;[32] an iodo-silver benzoate complex is reported by C. Prévost[33] to be serviceable for the oxidation of ethylenic compounds to α-glycols; and selenium dioxide has been employed in the oxidation of aldehydes and ketones containing the group $\cdot CH_2\cdot CO\cdot$ to dicarbonyl compounds[34] and of olefins to aldehydes.[35]

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[30] M. S. Kharasch and F. R. Mayo, *J. Amer. Chem. Soc.*, 1933, **55**, 2468, 2521; *A.*, 805; M. S. Kharasch, M. C. McNab, and F. R. Mayo, *ibid.*, p. 2531; *A.*, 805.

[31] *Annalen*, 1930, **481**, 263; *A.*, 1930, 1278; *Ber.*, 1931, **64**, [*B*], 260; *A.*, 1931, 461.

[32] L. Malaprade, *Compt. rend.*, 1928, **186**, 382; *A.*, 1928, 269; *Bull. Soc. chim.*, 1928, [iv], **43**, 683; *A.*, 1928, 867; P. Fleury and J. Lange, *Compt. rend.*, 1932, **195**, 1395; *A.*, 1933, 376; *J. Pharm. Chim.*, 1933, [viii], **17**, 313; *A.*, 591; P. Fleury and R. Paris, *Compt. rend.*, 1933, **196**, 1416; *A.*, 696.

[33] *Compt. rend.*, 1933, **196**, 1129; *A.*, 711.

Ascorbic Acid.

In 1928 A. Szent-Györgyi isolated from adrenal cortex, oranges, and cabbages a highly reactive crystalline substance, $C_6H_8O_6$, which on account of its acidic character and its resemblance to the carbohydrates in reducing power and colour reactions was named hexuronic acid.[36] This substance, which is widely distributed in plants and animals, was found to possess strong antiscorbutic properties[37] and subsequently aroused great interest as the possibility became apparent that it might represent the antiscorbutic factor of vegetable and animal materials (vitamin C) in pure crystalline condition. Its constitution and behaviour have been extensively investigated, but owing to the complexity of the problem presented by its biological activity its uniqueness as an antiscorbutic agent has not been finally established.[38]

Szent-Györgyi's compound is not a member of the uronic acid class and has been renamed ascorbic acid.[39] It is a weak acid which does not lactonise, and since it gives salts of the type $C_6H_7O_6M$ it cannot itself be a lactone of an acid $C_6H_{10}O_7$. That at least five of the six carbon atoms are present as an unbranched chain is shown by the fact that it yields furfuraldehyde quantitatively on treatment with boiling hydrochloric acid;[40] that it is enolic and probably contains no free aldehyde group is shown by the intense colour developed with ferric chloride and by the failure to give a colour with Schiff's reagent, respectively. With phenylhydrazine it yields a diphenylhydrazone, and with other ketonic reagents analogous derivatives.[40, 41] Its most characteristic property, however, and one that is probably largely responsible for its biological activity, is its ability to undergo reversible oxidation. It is immediately attacked in cold neutral or acid solution by aqueous iodine, ozone, silver nitrate, copper acetate, and permanganate, and in alkaline solution by gaseous oxygen and sodium hypoiodite. The reaction with aqueous iodine, first observed by Szent-Györgyi, was at an early stage pictured as proceeding in the manner :

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[34] H. L. Riley, J. F. Morley, and N. A. C. Friend, *J.*, 1932, 1875; *A.*, 1932, 833.

[35] H. L. Riley and N. A. C. Friend, *ibid.*, p. 2342; *A.*, 1932, 1108.

[36] *Biochem. J.*, 1928, **22**, 1387; *A.*, 1929, 98.

[37] J. L. Svirbely and A. Szent-Györgyi, *Nature*, 1932, **129**, 576, 690; *A.*, 1932, 548, 657; *Biochem. J.*, 1932, **26**, 865; *A.*, 1932, 886; *ibid.*, 1933, **27**, 279; *A.*, 541; T. W. Birch, L. J. Harris, and S. N. Ray, *Nature*, 1933, **131**, 273; *A.*, 433; J. Tillmans, P. Hirsch, and R. Vaubel, *Z. Unters. Lebensm.*, 1933, **65**, 145; *A.*, 433.

[38] For a summary of the evidence regarding the relationship to vitamin C, see A. Szent-Györgyi, *Nature*, 1933, **131**, 225; *A.*, 433.

[39] W. N. Haworth and A. Szent-Györgyi, *ibid.*, p. 24; *A.*, 196.

[40] E. G. Cox, E. L. Hirst, and R. J. W. Reynolds, *ibid.*, 1932, **130**, 888; *A.*, 1933, 100.

[41] P. Karrer, H. Salomon, K. Schöpp, and R. Morf, *Helv. Chim. Acta*, 1933, **16**, 181; *A.*, 490.

$$\left.\begin{array}{ll} \text{(LXIX.)} & HO_2C\cdot CO\cdot CO\cdot CH_2\cdot CH(OH)\cdot CH_2\cdot OH \\ & \qquad\qquad\qquad\textit{or} \\ \text{(LXX.)} & HO_2C\cdot CO\cdot C(OH){:}CH\cdot CH(OH)\cdot CH_2\cdot OH \end{array}\right\} \underset{2HI}{\overset{I_2 + aq.}{\rightleftharpoons}} \begin{array}{c}\text{Oxidation}\\ \text{product}\end{array}$$

where the forward reaction resulted in oxidation, as though at a double bond, by one atomic proportion of oxygen (or alternatively, dehydrogenation by loss of two atomic proportions of hydrogen), and the reverse reaction in reduction by the hydriodic acid generated in the forward reaction.[40, 42] The formulæ here ascribed to ascorbic acid contain a free carboxyl group. Other alternative formulæ of the type $HO\cdot CH_2\cdot CH(OH)\cdot CO\cdot CH_2\cdot CO\cdot CO_2H$ (LXXI), which were almost simultaneously suggested by P. Karrer[43, 44] (including various tautomeric ring forms), also contain a free carboxyl group.

The oxidation product obtained with iodine can be reduced to ascorbic acid by hydrogen sulphide[43] as well as by hydriodic acid. It differs, however, from ascorbic acid in no longer yielding furfuraldehyde on treatment with hydrochloric acid.[45] Since it was found to be neutral in reaction and to behave as the lactone of a monobasic hydroxy-acid, there appeared good reason for believing that ascorbic acid itself contains no free carboxyl group and that its acidic properties are due to a dissociating hydroxyl group.[45] The latter would in all probability form part of a reactive group of the type $\cdot C(OH){:}C(OH)\cdot$, such as occurs in dihydroxymaleic acid.[42, 46] Support is lent to this view by the close parallel that can be drawn between dihydroxymaleic acid and ascorbic acid as regards (1) their reversible oxidisability with aqueous iodine, (2) the notable change which occurs in the absorption spectrum of each as oxidation proceeds,[47] and (3) the capacity of the enolic groups for methyl-

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[42] W. N. Haworth, *J. Soc. Chem. Ind.*, 1933, **52**, 482; *A.*, 698.

[43] P. Karrer, H. Salomon, R. Morf, and K. Schöpp, *Biochem. Z.*, 1933, **258**, 4; *A.*, 490.

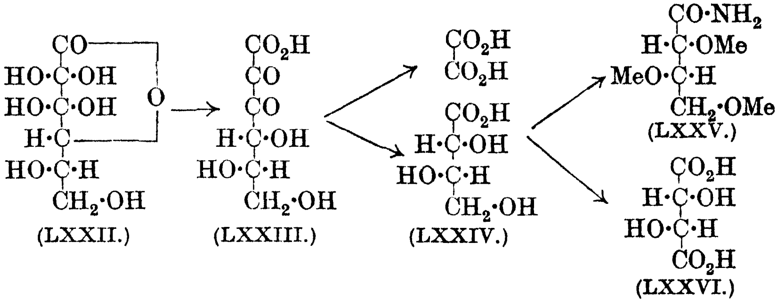
[44] P. Karrer, G. Schwarzenbach, and K. Schöpp, *Helv. Chim. Acta*, 1933, **16**, 302; *A.*, 490.

[45] E. L. Hirst, *J. Soc. Chem. Ind.*, 1933, **52**, 221; *A.*, 489.

[46] H. von Euler and C. Martius, *Arkiv Kemi, Min. Geol.*, 1933, **11**, [*B*], 1; *A.*, 699. These authors have suggested the occurrence of the $\cdot C(OH){:}C(OH)\cdot$ group from analogies with gluco-reductone, $CHO\cdot C(OH){:}CH(OH)$, which closely resembles ascorbic acid in several important respects.

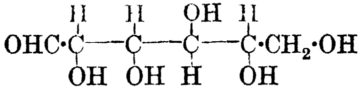
[47] R. W. Herbert and E. L. Hirst, *Nature*, 1932, **130**, 205; *A.*, 1932, 982.

ation by diazomethane,[41, 48] giving derivatives whose absorption spectra stand in similar close relationship with those of the parent substances.[42] The oxidation product obtained with aqueous iodine undergoes further oxidation with alkaline sodium hypoiodite (1 mol.) to yield, quantitatively, oxalic acid and a trihydroxybutyric acid (LXXIV).[40] The latter substance, *l*-threonic acid, was recognised in the form of the crystalline amide of its methyl derivative, which proved to be trimethyl *l*-threonamide (LXXV);[40] in addition, the trihydroxybutyric acid itself was found to yield *d*-tartaric acid (LXXVI) on oxidation with nitric acid.[45] Ascorbic acid also yields *l*-threonic acid on oxidation with acid permanganate.[40]



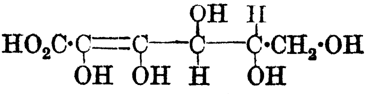
(LXXII.) (LXXIII.) (LXXIV.) (LXXV.) (LXXVI.)

The above observations show that ascorbic acid is a derivative of *l*-gulose (LXXVII), and that the lactonic first oxidation product, which carefully conducted methylation experiments have now



$$OHC\cdot\overset{H}{\underset{OH}{C}}-\overset{H}{\underset{OH}{C}}-\overset{OH}{\underset{H}{C}}-\overset{H}{\underset{OH}{C}}\cdot CH_2\cdot OH$$

(LXXVII.)



$$HO_2C\cdot\underset{OH}{C}=\underset{OH}{C}-\overset{OH}{\underset{H}{C}}-\overset{H}{\underset{OH}{C}}\cdot CH_2\cdot OH$$

(LXXVIII.)

shown to have the structure (LXXII), must be capable of reacting in the form (LXXIII) (2 : 3-diketo-*l*-gulonic acid). The evidence also indicates that the first oxidation product is a lactone of (LXXIII) the carbonyl groups being in all probability hydrated.[49, 42] Ascorbic acid is the reduction product of this lactone and should, in view of its enolic character, be represented as a lactone of the acid (LXXVIII) (3-keto-*l*-gulonolactone).

The methylation of ascorbic acid can be carried out in two stages. By the action of diazomethane methyl groups can be introduced at the enolic centres : in this way the dimethyl derivative (LXXIX)

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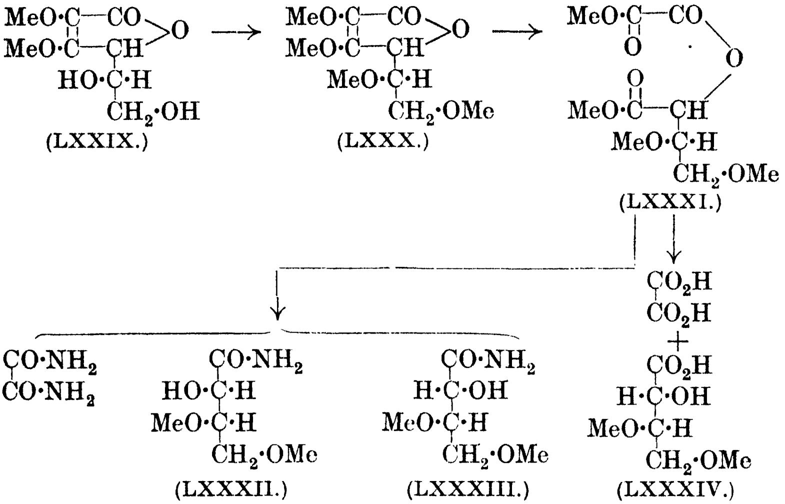
[48] F. Micheel and K. Kraft, *Z. physiol. Chem.*, 1933, **215**, 215; *A.*, 489.

[49] E. L. Hirst, E. G. V. Percival, and F. Smith, *Nature*, 1933, **131**, 617; *A.*, 594.

is obtained.[50] Two other hydroxyl groups can be methylated by Purdie's reagents, giving tetramethyl ascorbic acid (LXXX).[49]



(LXXIX.) (LXXX.) (LXXXI.)

(LXXXII.) (LXXXIII.) (LXXXIV.)

This substance reacts with ozone, two atoms of oxygen being added on with formation of a neutral product (LXXXI)[49] which has been identified as an α-oxalyl derivative of 3 : 4-dimethyl *l*-threonate. An analogous ozonolytic degradation has been carried out on di-*p*-nitrobenzoyl dimethyl ascorbic acid.[48]

The identification of the neutral ester (LXXXI) depends on its hydrolysis (*a*) with methyl-alcoholic ammonia to yield oxamide and 3 : 4-dimethyl *l*-threonamide (LXXXIII), and (*b*) with barium hydroxide to yield barium oxalate and the barium salt of 3 : 4-dimethyl *l*-threonic acid (LXXXIV).[49] In each of these hydrolyses, however, the derivative of 3 : 4-dimethyl *l*-threonic acid was accompanied by a small quantity of its epimeride, *viz.*, 3 : 4-dimethyl erythronamide (LXXXII), and barium 3 : 4-dimethyl *l*-erythronate[51] respectively. The free 3 : 4-dimethyl *l*-threonic acid (LXXXIV)

[50] The compound which this substance forms with alcoholic ammonia was not at first recognised as the amide

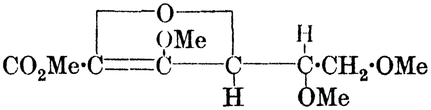
$$[HO{\cdot}CH_2{\cdot}CH(OH){\cdot}CH(OH){\cdot}C(OMe){:}C(OMe){\cdot}CO{\cdot}NH_2],$$

which might normally be expected to arise by ammoniolytic fission of the lactone ring.

[51] The origin of the epimerides is obscure. Apparently inversion of the groups attached to C_4 of the original ascorbic acid occurs at some point during methylation or ozonolysis—probably by the action of the alkali employed in the decomposition of the ozonide. The possibility that the ascorbic acid used contained two isomerides is rejected on the ground that no trace of *i*-tartaric acid has been detectable in the *d*-tartaric acid arising by direct oxidation of *l*-ascorbic acid.

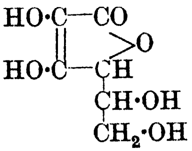
yields on methylation methyl 2 : 3 : 4-trimethyl *l*-threonate, and this is convertible into the same crystalline amide (LXXV) which had previously been derived by oxidation of ascorbic acid and methylation of the *l*-threonic acid so obtained.[52]

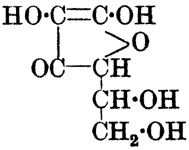
Since no loss of carbon atoms occurs in the degradation of tetramethyl ascorbic acid (LXXX) to the open-chain oxalyl derivative (LXXXI), there can be no doubt that the former of these compounds contains a ring system; furthermore, the nature of the reaction leaves open only two possibilities for the structure of this compound, *viz.*, (LXXX) and (LXXXV). The latter, however, contains a propylene oxide ring, and is inherently improbable owing to the strained nature of such a ring : in addition, the properties of ascorbic acid, and the fact that its primary oxidation product is a lactone and not an acid, provide decisive evidence in favour of (LXXX).[52]

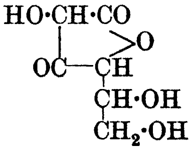

(LXXXV.)

The fact that dimethyl ascorbic acid is a neutral substance which reacts with one equivalent of sodium hydroxide to give a sodium salt was regarded by Karrer[41] and by F. Micheel[53] and their collaborators as proof that one of the methoxyl groups is of ester character. It is found, however, that the sodium salt is formed without elimination of methyl alcohol and proceeds in the cold in a manner similar to the opening of a lactone ring.[49] Tetramethyl ascorbic acid has, then, the structure (LXXX) and the form of ascorbic acid which reacts with diazomethane must be (LXXXVI).[52]

Various tautomeric modifications of this structure (LXXXVI) are possible, *e.g.*, (LXXXVII) and (LXXXVIII), and it is suggested that the potential mobility of constitution plays a part in the special reactivity of ascorbic acid. Two of these forms at least, (LXXXVIII) and (LXXXIX), should give rise to stereoisomerides, but no such modifications have been observed, and indeed the


(LXXXVI.)


(LXXXVII.)


(LXXXVIII.)

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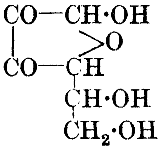
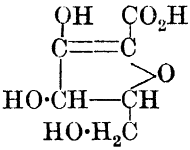
[52] R. W. Herbert, E. L. Hirst, E. G. V. Percival, R. J. W. Reynolds, and F. Smith, *J.*, 1933, 1270; *A.*, 1143.

[53] F. Micheel and K. Kraft, *Z. physiol. Chem.*, 1933, **216**, 233; *A.*, 698.

spatial configuration of such forms cannot be reconciled with the *X*-ray data of E. G. Cox,[54] which require an extraordinarily flat molecule. The close similarity between the absorption spectra of ascorbic acid and its dimethyl derivative, taken in conjunction with the similar relationship existing in the dihydroxymaleic acid series, affords strong indication that in solution, whether in acid, neutral, or alkaline media, ascorbic acid is essentially in the condition represented by (LXXXVI) (enolic form of 3-keto-*l*-gulofuranolactone).[52] The stability of this structure under the different conditions is a feature which further investigation will doubtless explain; possibly the stability of the lactone ring in the free acid may be in some way connected with the ionised condition of the hydroxyl group responsible for salt formation, for, when the reactive hydroxyl group is methylated, the lactone ring is opened readily by cold dilute alkali.[52]

(LXXXIX.)





(XC.)

The *X*-ray data of Cox [54] reveal that the formula (LXXXVI) of Hirst and his collaborators accounts satisfactorily for the crystallographic properties of ascorbic acid; moreover, a model of the molecule shows that, out of the total of twelve carbon and oxygen atoms, all but one can be accommodated in the same plane without appreciable valency strain, whilst the remaining carbon atom (C_5) lies less than 1 Å. above the plane. A hydrofuran type of formula (XC) advocated by Micheel and Kraft, and later put forward by Karrer as an alternative to (LXXI), does not accord with the crystallographic and *X*-ray measurements for ascorbic acid; [55] moreover, the first oxidation product derived from a substance of this formula would have a free carboxyl group, the properties of its dimethyl derivative would be different from those observed, and ozonisation of the tetramethyl derivative would yield a product giving on hydrolysis oxalic acid and 2 : 4-dimethyl *l*-threonic acid instead of the 3 : 4-dimethyl *l*-threonic acid actually obtained.

Various derivatives of ascorbic acid have played an important part in the discussion of the constitution of this substance, and Hirst and his collaborators show that these can readily be related to formula (LXXXVI). The monoacetone derivative of L. von

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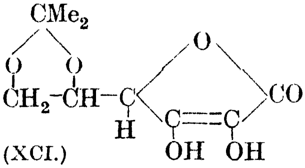
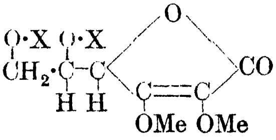
[54] *Nature*, 1932, **130**, 205; *A.*, 1932, 987.

[55] E. G. Cox and E. L. Hirst, *ibid.*, 1933, **131**, 402; *A.*, 490.

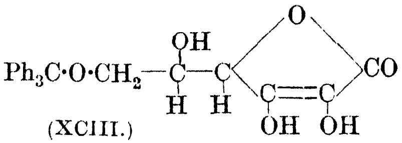
Vargha,[56] which Karrer and his collaborators[43] found to be convertible without loss of enolic character into dimethyl monoacetone ascorbic acid by means of diazomethane, must be represented by (XCI). Similarly Micheel and Kraft's di-*p*-nitrobenzoyl derivative



(XCI.)



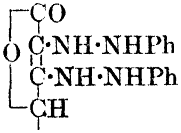
(XCII.)

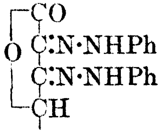


(XCIII.)

is to be represented by (XCII) ($X = \cdot CO \cdot C_6H_4 \cdot NO_2$), and Vargha's triphenylmethyl derivative by (XCIII); and the former of these formulæ accounts satisfactorily for the conversion of the di-*p*-nitrobenzoyl derivative into oxalic acid and *l*-threonic acid by ozonolysis, followed by hydrolysis. The preparation of diphenylhydrazones has been referred to above: the possibilities for structural isomerism and stereoisomerism in the formation of these derivatives from ascorbic acid and its reversible oxidation product are so numerous that the allocation of precise structures is a matter of extreme difficulty. The highly coloured nature of the ascorbic acid derivatives renders it doubtful whether a true osazone structure is present. The analytical data point to a condensation product derived from $C_6H_8O_6$ rather than from $C_6H_6O_6$, but with phenylhydrazones it is difficult to discriminate by analysis between formulæ so closely related. On the basis of the formula $C_6H_8O_4(N \cdot NHPh)_2$ Hirst and his collaborators[52] suggest that a red derivative, m. p. 187°, which is obtainable from ascorbic acid is possibly (XCIV). An orange

(XCIV.)





(XCV.)

derivative, m. p. 216°, which appears to arise from the lactone form of the oxidised substance may well be a true osazone (XCV), and a yellow derivative, m. p. 210°, prepared from an aqueous solution of the oxidised substance which has been allowed to stand, is probably to be regarded as an osazone which is formed from the open-chain form of the oxidation product and subsequently lactonised.

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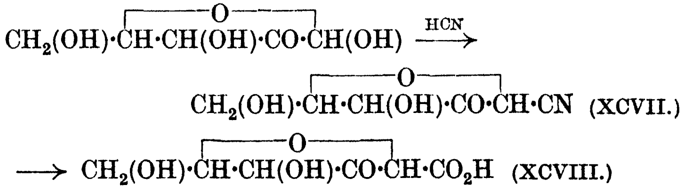
[56] *Nature*, 1932, **130**, 846; *A.*, 1933, 53.

The foregoing suggestions as to the constitutions of the diphenylhydrazones are based on a detailed study of the rotation and absorption spectrum of the oxidation product of ascorbic acid in acid and in alkaline solution.[52] The aqueous solution of the oxidation product changes in rotation on keeping, and increases in acidity until at least 80% of the product is present as free acid (doubtless LXXIII). No disintegration of the molecule, however, occurs in this change, since reduction of the final material gives ascorbic acid in good yield. Alkaline solutions of the oxidation product are yellow, and extraordinarily unstable in the presence of oxidising agents, including gaseous oxygen. The changes which take place are complex, but to a small extent self-oxidation and reduction of the oxidation product with partial regeneration of ascorbic acid occurs.

Synthesis.—Before the constitution of ascorbic acid, as represented by formula (LXXXVI), became generally accepted, T. Reichstein, A. Grüssner, and R. Oppenauer [57] announced a synthesis of *d*-ascorbic acid based on a short series of reactions starting from xylosone. Under the impression that ascorbic acid possessed the hydrofuran formula (XC), these authors submitted a crude xylosone preparation to the action of hydrogen cyanide and hydrolysed the resulting nitrile : the hydrolysis product yielded an acetone derivative which in melting point and reducing power resembled the acetone derivative of ascorbic acid. The synthesis was represented as proceeding according to the scheme :



(XCVI.)
$$CH_2(OH)\cdot\overbrace{CH\cdot CH(OH)\cdot CO\cdot CH}^{O}(OH)\xrightarrow{HCN}$$
$$CH_2(OH)\cdot\overbrace{CH\cdot CH(OH)\cdot CO\cdot CH}^{O}\cdot CN$$
(XCVII.)
$$\longrightarrow CH_2(OH)\cdot\overbrace{CH\cdot CH(OH)\cdot CO\cdot CH}^{O}\cdot CO_2H$$
(XCVIII.)

and apart from the incorrectness of the formula (XCVIII) (the ketonised form of XC) ascribed to ascorbic acid, it is to be observed that Reichstein and his collaborators took for granted the possession of a particular furanose structure (XCVI) by xylosone and represented the reaction of the latter with hydrogen cyanide as proceeding in an unusual way. There can be no doubt, however, that the synthetic product obtained by them was a derivative of *d*-ascorbic acid and to the workers belongs the credit of having described the first synthetic derivative of the *d*-enantiomorph of natural ascorbic acid.

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[57] *Helv. Chim. Acta*, **1933**, **16**, **561**; *A.*, **594.**

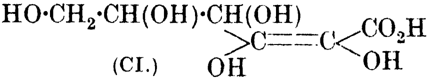
Meanwhile, however, Haworth and Hirst and their collaborators had independently begun work on the synthesis of both the *d*- and the *l*-form of ascorbic acid, and with this end in view had embarked on the preparation and the substantiation of the structure of the then unknown xylosone, as a preliminary to its conversion *via* the corresponding cyanohydrin into ascorbic acid.[52] The investigation of these authors led to the successful preparation of the *d*- and the *l*-form of xylosone and the conversion of these respectively into the *d*- and the *l*-form of ascorbic acid.[58] The xylosone (XCIX), on contact with potassium cyanide and calcium chloride, yielded the cyanohydrin (C), which suffered almost immediate hydrolysis to the keto-acid (CI). This acid, although capable of reducing acid iodine solution, does not possess the properties of ascorbic acid and has been designated *ψ*-ascorbic acid;

$$\mathrm{CH_2(OH)\cdot CH(OH)\cdot CH(OH)\cdot CO\cdot CHO} \xrightarrow{\mathrm{HCN}}$$

(XCIX.)

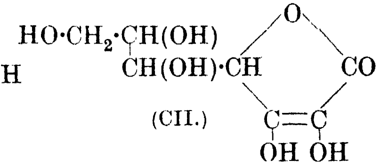
$$\mathrm{CH_2(OH)\cdot CH(OH)\cdot CH(OH)\cdot CO\cdot CH(OH)\cdot CN} \longrightarrow \mathrm{(LXXXVI)}$$

(C.)



$$\begin{matrix}\mathrm{HO\cdot CH_2\cdot CH(OH)\cdot CH(OH)} & & \mathrm{CO_2H}\\ & \mathrm{>C{=}C<} & \\ \mathrm{OH} & & \mathrm{OH}\end{matrix}$$

(CI.)



(CII.)

its conversion, however, into ascorbic acid proceeds quantitatively in the presence of dilute hydrochloric acid. As the result of the syntheses of both enantiomorphs of ascorbic acid in crystalline condition the representation of natural (*l*-) ascorbic acid by the formula (LXXXVI) receives strong experimental support.

By an analogous procedure Haworth and Hirst and their coworkers have obtained a crystalline product from glucosone possessing properties identical with those of ascorbic acid. To this product the constitution (CII) is assigned on the analogy of the structure which has been determined for ascorbic acid.

E. H. FARMER.

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[58] W. N. Haworth and E. L. Hirst, *J. Soc. Chem. Ind.*, 1933, **52**, 645; *A.*, 936; R. G. Ault, D. K. Baird, H. C. Carrington, W. N. Haworth, R. Herbert, E. L. Hirst, E. G. V. Percival, F. Smith, and M. Stacey, *J.*, 1933, 1419; *A.*, 1275; see also T. Reichstein, A. Grüssner, and R. Oppenauer, *Nature*, 1933, **132**, 280; *A.*, 1035; *Helv. Chim. Acta*, 1933, **16**, 1019; *A.*, 1143.

PART II.—HOMOCYCLIC DIVISION.

Intramolecular Rearrangements.

(Continued from *Ann. Reports*, 1930, **27**, 114.)

THE mechanism of intramolecular migrations of groups has been successfully interpreted on the assumption of a transfer of electrons within the system, just as in the simpler case of tautomerism. The conception has recently been modified [1] in that it is suggested that the group X (chlorine, oxygen, or other strongly negative atom or group), when it is removed from the system, takes with it a complete octet of electrons and leaves the atom to which it was attached with an " open sextet " :

$$:\overset{..}{\underset{..}{A}}:\overset{..}{\underset{..}{B}}:\overset{..}{\underset{..}{X}}: \longrightarrow :\overset{..}{\underset{..}{A}}:\overset{..}{\underset{..}{B}} + :\overset{..}{\underset{..}{X}}:$$

The subsequent changes undergone by the residue AB determine the course of the reaction : (1) it may take up a negative ion from the surrounding medium, giving the "normal" product ABY; (2) if the atom A carries a hydrogen atom, this may be lost as a proton and an unsaturated compound will result, A=B (or the proton may be removed from an atom in a more remote part of the molecule, giving rise to a cyclic structure); (3) if the atom B has a greater attraction for electrons than A, two electrons may be transferred from the latter, leaving it with an " open sextet." This electron transfer means the shifting of the group attached by means of these electrons, from A to B; the new residue will then recombine with the original negative ion X, or one taken from the medium, Y, to give the compound XAB or YAB. The net result is a rearrangement, by the transfer of either a hydrogen atom or a group, from A to B. This process is a unimolecular one, but the recombination of the residue AB with the negative ion is bimolecular. The reaction scheme given above applies not only to pinacolic rearrangements, but also to the Hofmann, Lossen, Curtius, and Beckmann changes; it is particularly helpful in interpreting such changes as the Wagner–Meerwein, where an alkyl group and a halogen atom change places in a fully saturated system.

In some reactions, the group X is removed as a positive ion with a sextet of electrons, leaving the atom B with an octet; in these cases *no* rearrangement can take place. An example of this is the Hofmann rearrangement of *tert.*-butylacetamide, which gives the normal product : [2]

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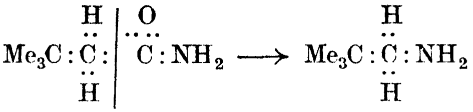
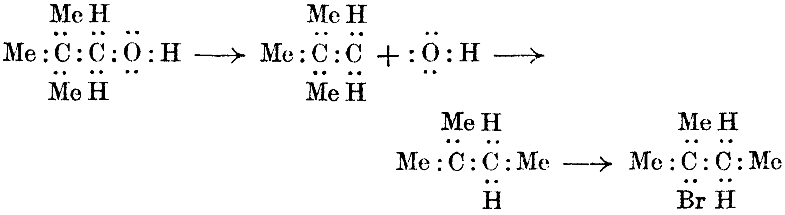
[1] F. C. Whitmore, *J. Amer. Chem. Soc.*, 1932, **54**, 3274; *A.*, 1932, 1016; F. C. Whitmore and E. E. Stahly, *ibid.*, 1933, **55**, 4153; *A.*, 1271; a short account has already appeared in *Ann. Reports*, 1932, **29**, 98.

[2] F. C. Whitmore and A. H. Homeyer, *ibid.*, p. 3435; *A.*, 1932, 1023.



$$\mathrm{Me_3C}:\overset{\mathrm{H}}{\underset{\mathrm{H}}{\ddot{\mathrm{C}}}}:\Big|\ \overset{\mathrm{O}}{\mathrm{C}}:\mathrm{NH_2}\longrightarrow \mathrm{Me_3C}:\overset{\mathrm{H}}{\underset{\mathrm{H}}{\ddot{\mathrm{C}}}}:\mathrm{NH_2}$$

The *neo*pentyl residue is here pictured as a negative radical. In other cases, such as the formation of halides from *neo*pentyl alcohol, in which the *neo*pentyl residue remains positive, rearrangement products are formed almost exclusively :[3]

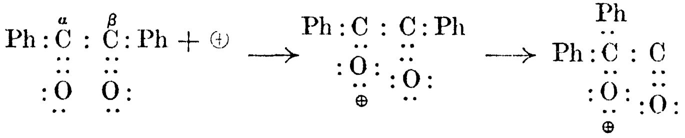


$$\mathrm{Me}:\overset{\mathrm{Me}}{\underset{\mathrm{Me}}{\mathrm{C}}}:\overset{\mathrm{H}}{\underset{\mathrm{H}}{\mathrm{C}}}:\ddot{\mathrm{O}}:\mathrm{H}\longrightarrow \mathrm{Me}:\overset{\mathrm{Me}}{\underset{\mathrm{Me}}{\mathrm{C}}}:\overset{\mathrm{H}}{\underset{\mathrm{H}}{\mathrm{C}}}+:\ddot{\mathrm{O}}:\mathrm{H}\longrightarrow$$

$$\mathrm{Me}:\overset{\mathrm{Me}}{\mathrm{C}}:\overset{\mathrm{H}}{\underset{\mathrm{H}}{\mathrm{C}}}:\mathrm{Me}\longrightarrow \mathrm{Me}:\overset{\mathrm{Me}}{\underset{\mathrm{Br}}{\mathrm{C}}}:\overset{\mathrm{H}}{\underset{\mathrm{H}}{\mathrm{C}}}:\mathrm{Me}$$

The application of these views has been illustrated in a number of papers dealing with rearrangements in aliphatic compounds.[4]

On the other hand, the benzilic acid change is interpreted by assuming the addition of a *positive* ion to the carbonyl group; the mechanism is thus the inverse of that proposed by C. K. Ingold :[5]



$$\mathrm{Ph}:\underset{:\ddot{\mathrm{O}}}{\overset{\alpha}{\mathrm{C}}}:\underset{\ddot{\mathrm{O}}:}{\overset{\beta}{\mathrm{C}}}:\mathrm{Ph}+\oplus\longrightarrow \mathrm{Ph}:\underset{\underset{\oplus}{:\ddot{\mathrm{O}}:}}{\mathrm{C}}:\underset{:\ddot{\mathrm{O}}:}{\mathrm{C}}:\mathrm{Ph}\longrightarrow \mathrm{Ph}:\underset{\underset{\oplus}{:\ddot{\mathrm{O}}:}}{\overset{\mathrm{Ph}}{\mathrm{C}}}:\underset{:\ddot{\mathrm{O}}:}{\mathrm{C}}$$

Addition of hydroxyl at C_β of the rearranged product then gives benzilic acid; it is difficult to see why the change requires the presence of alkali (a source of *negative* hydroxyl ions), and not of acids.*

There appears to be some danger that hypotheses of this kind, helpful though they are in interpreting the course of numerous reactions, may be too widely generalised and it is well to recognise their limitations. For instance, there are changes which cannot be satisfactorily reconciled with an ionic mechanism, and of these the

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[3] F. C. Whitmore and H. S. Rothrock, *J. Amer. Chem. Soc.*, 1932, **54**, 3431; *A.*, 1932, 1017.

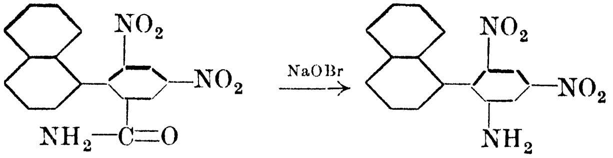
[4] F. C. Whitmore with D. P. Langlois, *ibid.*, pp. 3438, 3441; with A. R. Lux, *ibid.*, p. 3449; with A. L. Houk, *ibid.*, p. 3714; with K. C. Laughlin, *ibid.*, p. 4011; *A.*, 1932, 1016, 1022, 1023, 1109, 1232; with H. S. Rothrock, *ibid.*, 1933, **55**, 1106; with J. M. Church, *ibid.*, p. 1119; with W. L. Evers, H. S. Rothrock, H. M. Woodburn, and E. E. Stahly, *ibid.*, p. 1136; with D. P. Langlois, *ibid.*, p. 1518; with P. A. Krueger, *ibid.*, p. 1528; *A.*, 486, 486, 485, 695, 591.

[5] *Ann. Reports*, 1928, **25**, 124.

* The Reporter wishes to thank Prof. C. K. Ingold for drawing his attention to this point.

Hofmann rearrangement of the optically active amide (I) to an active amine (II) constitutes an important example :[6]

(I.)

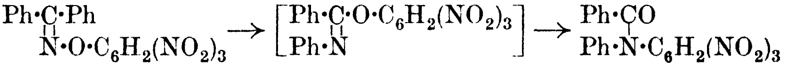


(II.)

The activity of the original compound is due to restricted rotation, owing to the steric effect of the carbamyl and the nitro-group in the *o*-positions; the blocking effect of these never ceases, as would doubtless be the case if the migrating group were to leave the system as an ion prior to its transfer to the nitrogen atom. The change evidently takes place by the establishment of a link between the migrating group and the nitrogen atom *before* the ultimate transfer of the bonding electrons, and not by the removal of the group as an ion, followed by recombination with another ion. The same mechanism would of course explain the formation of a " normal " product from *tert.*-butylacetamide.

It has also been shown [7] that in the Lossen rearrangement of some active hydroxamic acids, optical activity is preserved, but this can equally well be interpreted by the ionic mechanism.

The analogy existing between the Wagner–Meerwein rearrangement and the Beckmann change in oximes has recently been emphasised by A. W. Chapman and C. C. Howis,[8] who have examined the change in the picryl ethers of oximes :



$$\begin{array}{l}Ph{\cdot}C{\cdot}Ph\\ \quad\|\\ \quad N{\cdot}O{\cdot}C_6H_2(NO_2)_3\end{array} \rightarrow \left[\begin{array}{l}Ph{\cdot}C{\cdot}O{\cdot}C_6H_2(NO_2)_3\\ \quad\|\\ Ph{\cdot}N\end{array}\right] \rightarrow \begin{array}{l}Ph{\cdot}CO\\ \quad|\\ Ph{\cdot}N{\cdot}C_6H_2(NO_2)_3\end{array}$$

This unimolecular change proceeds spontaneously on heating in solution, is favoured by solvents of high dielectric constant, and is evidently limited to esters of strong acids (such as picric acid in this instance), in which respects it bears a strong resemblance to the Wagner–Meerwein change. The authors nevertheless prefer to regard the mechanism of the change as a purely intramolecular one, in which no separation of the rearranging group takes place.

Finally, it has been shown [9] that the benzidine change is an intramolecular process. Although the rearrangements of 2 : 2′-dimethoxy- and 2 : 2′-diethoxy-hydrazobenzene proceed at comparable rates, giving the corresponding 3 : 3′-benzidines, no trace of a mixed benzidine (3-methoxy-3′-ethoxy-) is formed when an equimolecular mixture of the two initial materials is subjected to rearrangement; this would certainly be expected if a separation of the migrating group as a free ion took place.

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[6] E. S. Wallis and W. W. Moyer, *J. Amer. Chem. Soc.*, 1932, **55**, 2598; *A.*, 821.

[7] E. S. Wallis and R. D. Dripps, *ibid.*, p. 1701; *A.*, 606; compare A. McKenzie and (Miss) E. R. L. Gow, *J.*, 1933, 705; *A.*, 822.

[8] *J.*, 1933, 806; *A.*, 952.

[9] C. K. Ingold and H. V. Kidd, *ibid.*, p. 984; *A.*, 1044.

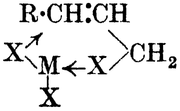
The addition of hydrogen chloride to vinylacetylene [10] gives the product (III), which is sufficiently stable to be converted into the carbinol, from which it can be obtained again by the action of hydrogen chloride; it is, however, isomerised to chloroprene (IV) by cuprous chloride in hydrochloric acid : the iodide corresponding to (III) is spontaneously isomerised on distillation.

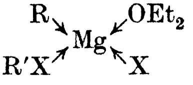
$$\mathrm{CH{:}C{\cdot}CH{:}CH_2} \xrightarrow{\mathrm{HCl}} \underset{\text{(III.)}}{\mathrm{CH_2{:}C{:}CH{\cdot}CH_2Cl}} \longrightarrow \underset{\text{(IV.)}}{\mathrm{CH_2{:}CCl{\cdot}CH{:}CH_2}}$$

The formation of (III) is clearly a case of 1 : 4-addition ; this cannot proceed by way of 1 : 2-addition, followed by anionotropic change, since (IV) and not (III) is the final stable product. Moreover, (III) reacts with Grignard reagents, forming products derived mostly from (IV); but here again, previous isomerisation cannot be the cause, since (IV) does not react with Grignard reagents.

The authors show that none of the current hypotheses based on ionisation can explain these reactions; they prefer to regard them as purely intramolecular and assume the intermediate production of a co-ordination complex. They point out that in $\alpha\gamma$-migrations of halogens the halogen atom on C_α approaches sufficiently closely to the γ-carbon atom for migration to occur—a process which is facilitated by the polarisation due to the unshared electrons of the halogen atom; finally, a bond is established. The relative ease of migration of the halogens is in the order I > Br > Cl, which accords well with this conception, the ready migration of iodine being due to the large effective diameter of the atom. The action of cuprous chloride on the chloride (III) is attributed to the formation of a complex such as (V) : *

(V.)





(VI.)

The same hypothesis explains the action of the Grignard reagent on (III); the groups R and R′ in the complex (VI) are practically in the form of cation and anion respectively and probably approach sufficiently close to one another for interaction without ever becoming free *ions*.

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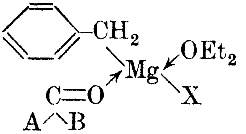
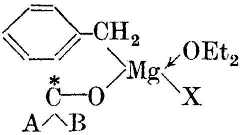
[10] W. H. Carothers and G. J. Berchet, *J. Amer. Chem. Soc.*, 1933, **55**, 2807; *A.*, 930.

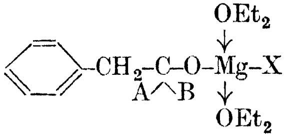
* The notation is that used by the authors.

Such a mechanism appears to fit in with the many observed cases of isomeric changes not leading to a true equilibrium.

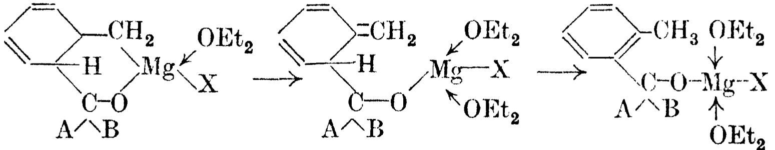
A similar view is taken by J. R. Johnson [11] in explaining the formation of *o*-tolyl derivatives from benzylmagnesium chloride and carbonyl compounds.[12] The first step is the formation of the complex (VII), in which a shift of electrons in the triad system Mg←O:C then causes either the normal or the abnormal reaction :


(VII.)

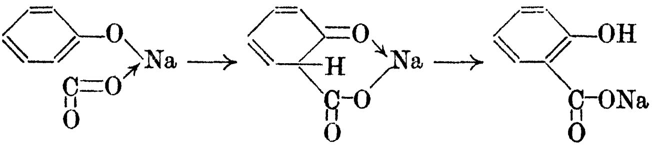

(VIII.)


(IX.)

In the first case, the electron drift tends to leave the carbon atom marked * with a sextet of electrons (VIII) ; the octet is completed by the migration of the benzyl group with its bonding electrons, and the octet of the magnesium is completed by co-ordination with ether (IX). In the abnormal reaction, the octet of C* is completed at the expense of the *ortho* double bond of the phenyl group, through a cyclic structure (X) ; it is followed by the rupture of the bond between the CH_2 group and the magnesium atom :


(X.) (XI.) (XII.)

The nature of the atoms A and B will clearly influence the process ; this explains why formaldehyde tends to give an abnormal reaction product more than other aldehydes, whilst ketones, esters, etc., react normally ; and it is suggested that it accounts for the *C*-alkylation of enolates and for such reactions as the Reimer–Tiemann and Kolbe. The latter is formulated thus :



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[11] *J. Amer. Chem. Soc.*, 1933, **55**, 3029; *A.*, 963.

[12] P. R. Austin and J. R. Johnson, *ibid.*, 1932, **54**, 647; *A.*, 1932, 385; *Ann. Reports*, 1932, **29**, 146.

Pinacolic Changes.—A considerable volume of experimental work has lately been published by Tiffeneau and his collaborators.[13–34] An attempt is made to correlate both the "affinity capacity" and the "migratory capacity" of different groups with their structure (for a definition of these terms, see *Ann. Reports*, 1930, **27**, 114).

The former property not only is responsible for the mode of elimination of water from pinacols, but also determines the orientation of the addition of hypoiodous acid to unsaturated compounds of the type

$$CRR'{:}CR''R''' \longrightarrow CRR'(OH){\cdot}CR''R'''I$$

the hydroxyl invariably becoming attached to the carbon atom carrying groups with the least affinity capacity.

The general sequence in which alkyl and aryl groups (and hydrogen) can be arranged according to their effect in these reactions is that of their capacity for electron release,[35] although the order does not hold very strictly when alkyl groups are considered, thus :

$$Me > Pr > Bu > Et > H > CH_2Ph$$

Similar empirical sequences are given for different combinations of groups; these comprise several not given in *Ann. Reports, loc. cit.*

The correlation of affinity capacity with migratory capacity is no easy matter. For alkyl groups the migratory capacities are

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[13] M. Tiffeneau, *Bull. Soc. chim.*, 1931, [iv], **49**, 1595.

[14] M. Tiffeneau, (Mme.) J. Lévy, and P. Weill, *ibid.*, p. 1606; *A.*, 1932, 388.

[15] M. Tiffeneau and (Mme.) J. Lévy, *ibid.*, p. 1617; *A.*, 1932, 388.

[16] *Idem, ibid.*, p. 1661; *A.*, 1932, 389.

[17] M. Tiffeneau, (Mme.) J. Lévy, and P. Weill, *ibid.*, p. 1709; *A.*, 1932, 389.

[18] (Mme.) J. Lévy and R. Pernot, *ibid.*, p. 1721; *A.*, 1932, 389.

[19] *Idem, ibid.*, p. 1730; *A.*, 1932, 390.

[20] M. Tiffeneau and (Mme.) J. Lévy, *ibid.*, p. 1738; *A.*, 1932, 390.

[21] A. Orekhoff and M. Roger, *ibid.*, p. 1754; *A.*, 1932, 391.

[22] M. Tiffeneau, A. Orekhoff, and M. Roger, *ibid.*, p. 1757; *A.*, 1932, 391.

[23] (Mme.) J. Lévy and (Mme.) Dvoleitzka-Gombinska, *ibid.*, p. 1765; *A.*, 1932, 392.

[24] (Mme.) J. Lévy and A. Tabart, *ibid.*, p., 1776; *A.*, 1932, 392.

[25] M. Tiffeneau, (Mme.) J. Lévy, and P. Jullien, *ibid.*, p. 1788; *A.*, 1932, 393.

[26] P. Weill, *ibid.*, p. 1795; *A.*, 1932, 393.

[27] M. Tiffeneau and (Mme.) J. Lévy, *ibid.*, p. 1806; *A.*, 1932, 393.

[28] P. Weill, *ibid.*, p. 1811; *A.*, 1932, 393.

[29] (Mme.) J. Lévy and J. Sfiras, *ibid.*, p. 1823; *A.*, 1932, 394.

[30] *Idem, ibid.*, p. 1830; *A.*, 1932, 395.

[31] (Mme.) J. Lévy and R. Pernot, *ibid.*, p. 1838; *A.*, 1932, 363.

[32] M. Tiffeneau, A. Orekhoff, and (Mme.) J. Lévy, *ibid.*, p. 1840; *A.*, 1932, 395.

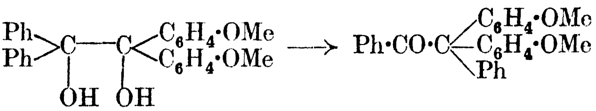
[33] M. Tiffeneau and (Mme.) J. Lévy, *ibid.*, p. 1847; *A.*, 1932, 395.

[34] M. Tiffeneau, *Compt. rend.*, 1932, **195**, 1284; *A.*, 384.

[35] C. K. Ingold, *Ann. Reports*, 1928, **25**, 134.

arranged in order of diminishing affinity capacities; and this is what might have been expected, since it is assumed that the ease of migration is governed by the strength of the bond by which the group is attached. Aryl groups, however, although possessing a high affinity capacity, invariably migrate more readily than alkyl groups and can be arranged in a sequence in which affinity capacity and migratory capacity go hand in hand. It is therefore clear that some additional factor is under observation.

W. E. Bachmann and F. H. Moser[36] have found it possible to evaluate quantitatively the relative migratory capacities of aryl groups in the rearrangement of symmetrical pinacols and to predict their behaviour in other cases, provided that compounds of the same type are used. These figures cannot, for instance, be applied to the rearrangement of unsymmetrical pinacols: W. E. Bachmann[37] finds that in pinacols of the type $Ph_2C(OH){\cdot}C(OH)Ar_2$ (where Ar = *m*-tolyl, *p*-tolyl, or anisyl) the anisyl group migrates less readily than phenyl. The anisyl group, although possessing the greatest migratory capacity, has also the greatest affinity capacity owing to its unshared electrons. The attachment of two such groups to one carbon atom of the pinacol therefore determines the preferential elimination of hydroxyl from that carbon and the migration of the phenyl group must inevitably follow:



$$Ph_2C(OH){-}C(OH)(C_6H_4{\cdot}OMe)_2 \longrightarrow Ph{\cdot}CO{\cdot}C(C_6H_4{\cdot}OMe)_2Ph$$

Essentially similar views are held by M. Migita,[38] who regards pinacolic changes as depending entirely on the "negativity," *i.e.*, the capacity for electron release, of the groups attached to the two hydroxylated carbons. The elimination of hydroxyl, which is the first stage, is facilitated by the attachment of negative groups; this explains why in unsymmetrical pinacols the less negative group migrates and in symmetrical pinacols the reverse is the case.

The migratory capacity of groups can be influenced by steric factors, for the *o*-anisyl group migrates less readily than *p*-anisyl, although their electron-releasing capacities should be the same;[39]

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[36] *J. Amer. Chem. Soc.*, 1932, **54**, 1124; *A.*, 1932, 515; see also W. E. Bachmann, *ibid.*, p. 1969; *A.*, 1932, 745.

[37] *Ibid.*, p. 2112; *A.*, 1932, 737; *ibid.*, 1933, **55**, 3857; W. E. Bachmann and H. R. Sternberger, *ibid.*, p. 3819; *A.*, 1159, 1163.

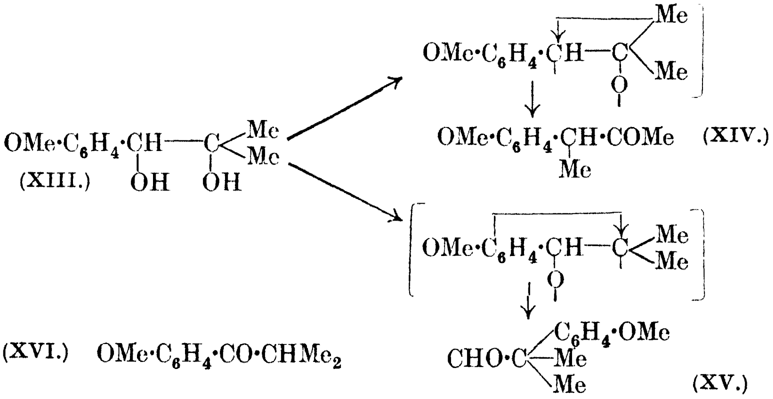
[38] *Bull. Chem. Soc. Japan*, 1932, **7**, 334, 341, 377, 382; 1933, **8**, 22, 27; *A.*, 68, 271, 394.

[39] C. H. Beale and H. H. Hatt, *J. Amer. Chem. Soc.*, 1932, **54**, 2405; *A.*, 1932, 854.

but *o*-anisyl migrates more readily than *m*-anisyl, the actual ratio being **3** : 2. This is attributed to a steric " ortho " effect of the substituent which varies with different groups : OMe>Me>Cl>Br ; this order is in good agreement with that theoretically deduced. The inertness of the 2 : 5-dimethoxyphenyl group is particularly noticeable, but in the 2 : 4-compound the additional methoxyl in the *p*-position, with its unshared electrons, to some extent overcomes the unfavourable effect of the *o*-group.

The work of Tiffeneau and his school has cleared up a number of difficult points with regard to the actual mechanism of pinacolic changes.

For instance, in the dehydration of glycols such as (XIII) two mechanisms are possible : the semipinacolic, by elimination of the secondary hydroxyl, and semihydrobenzoinic, followed by a rearrangement of the aldehyde produced by the reaction first observed by Danilov : [40]



The aldehyde (XV) has now been found to undergo the aldehydoketonic change, but it is the anisyl group which migrates and the ketone (XVI) produced is distinct from that obtained in the first reaction, which must therefore be a semipinacolic change.[18] The corresponding *m*-methoxy-glycol behaves in the same way,[18] and so does the next higher homologue, anisylmethylethylethyleneglycol.[26]

An even more convincing case is that of the optically active *o*-tolylhydrobenzoin (XVII) ; [41] dehydration under mild conditions gives an optically active ketone together with an inactive aldehyde (XIX). In the formation of the latter, the asymmetry of C_α is destroyed by the attachment of two similar groups; it cannot therefore be the intermediate product in the formation of the ketone (XVIII):

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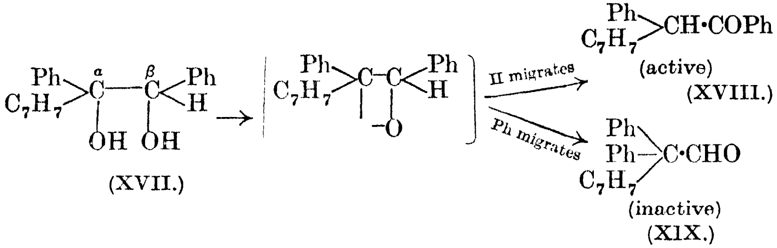
[40] *J. Russ. Phys. Chem. Soc.*, 1917, **49**, 282; 1919, **51**, 97.

[41] R. Roger and W. B. McKay, *J.*, 1933, 332; *A.*, 611.



(XVII.) (XVIII.) (XIX.)

The corresponding *p*-compound gave an inactive ketone [42] in addition to the isomeric ketone C_7H_7·CO·$CHPh_2$,[43] and the change was originally regarded as an example of vinyl dehydration.

In other cases the aldehydo-ketonic change, although giving rise to the same products as the semipinacolic mechanism, requires more drastic experimental conditions than those commonly used, or a different reagent,[24] but this is admittedly a less convincing argument and would not carry much weight but for the positive proof given above.

Similarly, it has been possible to establish the reality of the vinyl type of dehydration, in which no migration of groups occurs: [28]

$$\text{OMe}\cdot C_6H_4\cdot \text{CH(OH)}\cdot \text{C(OH)Me}\cdot C_6H_4\cdot \text{OMe} \longrightarrow \text{OMe}\cdot C_6H_4\cdot \text{CO}\cdot \text{CHMe}\cdot C_6H_4\cdot \text{OMe}$$

A somewhat similar mechanism is held to account for the dehydration of the unsaturated diol (XX) to tiglic aldehyde,[44] although an anionotropic mechanism (wandering of the OH group and subsequent elimination) is also possible:

$$\left.\begin{array}{l} CH_2(OH)\cdot CH{:}CMe\cdot CH_2\cdot OH \\ \qquad\qquad \text{or} \\ CH_2{:}CH\cdot CMe(OH)\cdot CH_2\cdot OH \end{array}\right\} \rightarrow CH_2{:}CH\cdot CMe{:}CH\cdot OH = CH_3\cdot CH{:}CMe\cdot CHO$$

(XX).

The migration of groups in aldehydo-ketonic transpositions does not appear to be governed by the same rules as that in pinacolic changes and no conclusions can safely be drawn from them. An attempt is being made to correlate the displacement of the ultraviolet absorption towards the visible spectrum with the stability to heat of glycols and of the aldehydes and ketones obtained from them on heating :[45]

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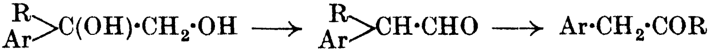
[42] A. McKenzie, R. Roger, and W. B. McKay, *J.*, 1932, 2597; *A.*, 1932, 1251; C. F. Koelsch, *J. Amer. Chem. Soc.*, 1932, **54**, 2049; *A.*, 1932, 746.

[43] A. McKenzie, A. K. Mills, and J. R. Myles, *Ber.*, 1930, **63**, [*B*], 904; *A.*, 1930, 788.

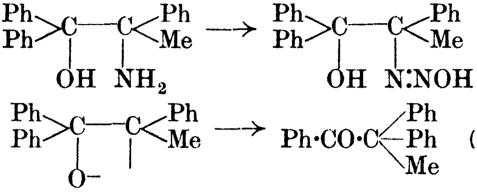
[44] A. F. Sheppard and J. R. Johnson, *J. Amer. Chem. Soc.*, 1932, **54**, 4385; *A.*, 47.



$$\overset{R}{\underset{Ar}{>}}C(OH)\cdot CH_2\cdot OH \longrightarrow \overset{R}{\underset{Ar}{>}}CH\cdot CHO \longrightarrow Ar\cdot CH_2\cdot COR$$

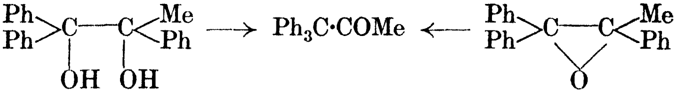
A new type of change, termed pinacolic deamination,[46] analogous to the semipinacolic deamination already described, has been realised :

(XXI.)



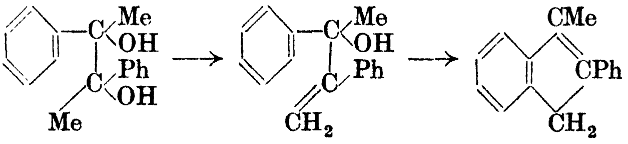
(XXII.)

As in the latter, the change appears to be governed by the position of the amino-group which is eliminated, and does not involve the intermediate production of the corresponding pinacol (XXIII), because the dehydration of the latter gives a product isomeric with (XXII), having the structure (XXIV). This pinacolin is also formed by the dehydration of the ethylene oxide (XXV), which occurs as a by-product in the deamination of (XXI) :



(XXIII.) (XXIV.) (XXV.)

An interesting side reaction in the dehydration of pinacols containing two or more phenyl groups leads to the formation of indenes; this has been found to proceed by way of a vinyl dehydration[47] and not as previously supposed :[48]



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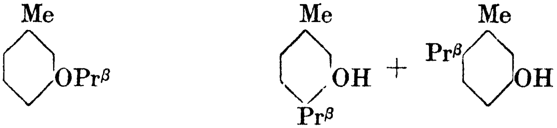
[45] (Mme.) Ramart-Lucas and J. P. Guerlain, *Bull. Soc. chim.*, 1931, [iv], **49**, 1860; (Mme.) Ramart-Lucas and P. Amagat, *ibid.*, 1932, [iv], **51**, 108; *A.*, 1932, 387, 505; (Mme.) Ramart-Lucas and F. Salmon-Legagneur, *ibid.*, p. 1069; *A.*, 1932, 1245.

[46] A. McKenzie and J. R. Myles, *Ber.*, 1932, **65**, [*B*], 209; *A.*, 1932, 382. Compare A. McKenzie and (Miss) E. M. Luis, *ibid.*, p. 794; *A.*, 1932, 746.

[47] O. Blum-Bergmann, *ibid.*, p. 109; *A.*, 1932, 273.

[48] A. Orekhoff and M. Tiffeneau, *Bull. Soc. chim.*, 1922, [iv], **31**, 253; *A.*, 1922, i, 458.

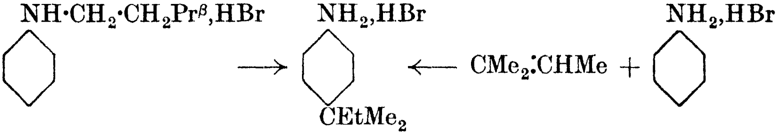
Other Rearrangements.—The rearrangement of phenolic ethers (Fries rearrangement) derived from *m*-cresol leads to both *o*- and *p*-alkylated phenols; thus, *m*-tolyl *iso*propyl ether yields, in addition to thymol (XXVI), the phenol (XXVII):[49]



(XXVI.) (XXVII.)

Tertiary alkyl groups migrate more readily than secondary ones, but those with a normal chain do not migrate at all. It can be calculated that the passage of the ethers into the isomeric alkylphenols involves a liberation of energy.[49] The migration of the unsaturated *iso*propenyl group gives mainly *o*-derivatives,[50] and *iso*butyl, *sec.*-butyl, and *tert.*-butyl phenyl ethers all give the same *p*-*tert.*-butylphenol[51] with aluminium chloride, the migrating group suffering isomerisation in the first two cases.

A similar isomerisation of the migrating group is also observed[52] in the rearrangement of *iso*amylamine hydrobromide, which leads to *p*-amino-*tert.*-amylbenzene, the same product being formed on heating aniline hydrobromide with trimethylethylene:



(XXVIII.) (XXIX.)

In addition, if the first reaction does not go to completion, some trimethylethylene can be isolated from the mixture, and it is therefore concluded that the production of this hydrocarbon is an intermediate step in the reaction. In the presence of certain metallic halides (XXVIII) is isomerised, not to (XXIX) but to the *iso*amyl compound, *i.e.*, the migrating radical is not rearranged. The formation of trimethylethylene cannot occur here, because this gives (XXVIII) under the same conditions. It is suggested that the two reactions follow a different course and cannot be due to the production of the same intermediate compound, such as an alkyl halide as suggested by Bennett and Chapman (*Ann. Reports*, 1930,

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[49] J. B. Niederl and S. Natelson, *J. Amer. Chem. Soc.*, 1932, **54**, 1063; *A.*, 1932, 510; R. A. Smith, *ibid.*, 1933, **55**, 849; *A.*, 389.

[50] J. B. Niederl and E. A. Storch, *ibid.*, p. 284; *A.*, 270.

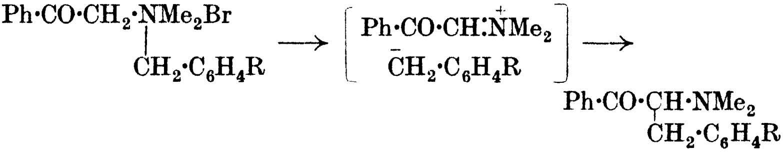
[51] R. A. Smith, *ibid.*, p. 3718; R. Baltzly and A. Bass, *ibid.*, p., 4292; *A.*, 1156, 1287.

[52] W. J. Hickinbottom, *J.*, 1932, 2396; *A.*, 1932, 1124.

27, 124). It must be confessed that such an explanation does not appear convincing; the case has some points of similarity with the reactions of the numerous *neo*pentyl compounds studied by Whitmore and his collaborators (p. 177) and could be interpreted on the same lines.

The migration of acyl groups in α-naphthyl esters gives both the 2- and the 4-acetylnaphthol;[53] it has also been studied in polyhydric phenols,[54] from which *o*- and *p*-derivatives are formed whenever possible.

T. Thomson and T. S. Stevens[55] have extended their investigations of the rearrangement of quaternary ammonium salts, in which a benzyl group migrates from nitrogen to an adjacent carbon, and have found that the relative migratory velocities of different substituted benzyl radicals are in the order $OMe > Me > Hals > NO_2$ and that this order holds for all three positions. The results are held to favour the reaction mechanism



$$\begin{matrix}\mathrm{Ph{\cdot}CO{\cdot}CH_2{\cdot}NMe_2Br}\\ |\\ \mathrm{CH_2{\cdot}C_6H_4R}\end{matrix} \longrightarrow \left[\begin{matrix}\mathrm{Ph{\cdot}CO{\cdot}CH{:}\overset{+}{N}Me_2}\\ \mathrm{\overset{-}{C}H_2{\cdot}C_6H_4R}\end{matrix}\right] \longrightarrow \begin{matrix}\mathrm{Ph{\cdot}CO{\cdot}CH{\cdot}NMe_2}\\ |\\ \mathrm{CH_2{\cdot}C_6H_4R}\end{matrix}$$

rather than that suggested in *Ann. Reports*, 1930, **27**, 123. The effect of substituents in the phenyl group of the phenacyl radical[56] is in agreement with such a view of the process; the instability of the intermediate ion is regarded as supplying the driving force of the reaction and must increase with the diminishing acidity of the methylene group of the phenacyl residue. Accordingly, the introduction of negative substituents into the phenyl group decreases the velocity of the change by increasing the acidity of the methylene group.

The analogous reaction

$$\mathrm{Ph{\cdot}CO{\cdot}CH_2{\cdot}S(CH_2Ph)MeBr} \longrightarrow \mathrm{Ph{\cdot}CO{\cdot}CH(CH_2Ph){\cdot}SMe}$$

has also been realised[57] and it is possible to cause the migration of a phenacyl group in the compound (XXX) or for a benzyl group to become attached to the methylene group of another benzyl in the compound (XXXI):[58]

$$\mathrm{Ph{\cdot}CO{\cdot}CH_2{\cdot}N(CH_2{\cdot}COPh)Me_2Br} \qquad \mathrm{Ph{\cdot}CH_2{\cdot}N(CH_2Ph)Me_2Br}$$

(XXX.) (XXXI.)

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[53] H. Lederer, *J. pr. Chem.*, 1932, [ii], **135**, 49; *A.*, 1932, 1251.

[54] F. Mauthner, *ibid.*, 1933, [ii], **136**, 205; *A.*, 395.

[55] *J.*, 1932, 55; *A.*, 1932, 262.

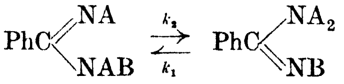
[56] J. L. Dunn and T. S. Stevens, *ibid.*, p. 1926; *A.*, 1932, 816.

[57] T. Thomson and T. S. Stevens, *ibid.*, p. 69; *A.*, 1932, 262.

[58] *Idem, ibid.*, p. 1932; *A.*, 1932, 854.

in the corresponding benzyl allyl compound it is only the benzyl group which migrates.

New evidence is also forthcoming on the rearrangement of triarylamidines :[59]

(XXXII.)  (XXXIII.)

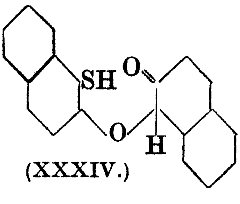
$$\mathrm{PhC}\begin{matrix}\diagup\mathrm{NA}\\ \diagdown\mathrm{NAB}\end{matrix}\ \overset{k_2}{\underset{k_1}{\rightleftarrows}}\ \mathrm{PhC}\begin{matrix}\diagup\mathrm{NA_2}\\ \diagdown\mathrm{NB}\end{matrix}$$

(A and B = aryl groups)

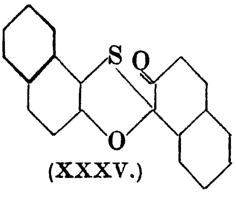
The series examined includes all the possible 3 : 5-dichloro-substituted compounds (A = Ph ; B = $C_6H_4Cl_2$, and the converse) and a comparison of the results with those previously obtained [60] shows that when group A remains the same, changes in group B have little influence on the velocity of the change (XXXII) to (XXXIII), but the velocities of the reverse change, k_1, vary appreciably. The changes in B therefore influence the reaction only when B is attached to the doubly bound nitrogen atom (as in XXXIII), which accords well with the authors' view that the change is initiated by the attraction exercised by the lone electrons of this nitrogen on the group which eventually migrates. This attraction can obviously be modified by substitution in group B ; thus, if B is replaced by a group with a greater affinity for electrons, the velocity of the change is decreased and vice versa.

S. Smiles and his collaborators have extended their work on the rearrangement of *iso*-β-naphthol sulphide (*Ann. Reports*, 1930, **27**, 122). It is suggested that in this change the negative character of the sulphur atom is the essential factor—hence the facilitating effect of alkali on the change and the inability of the corresponding *iso*sulphone to undergo a similar transformation.[61]

The *iso*sulphide is readily oxidised to a cyclic quinol (XXXIV) and it is thought probable that it is the ketonic form (XXXV) which undergoes rearrangement; this is supported by the stability to alkali of the corresponding *O*-methyl ether, which cannot, of course, give rise to a ketonic form, apart from the electron-repelling nature of the methyl group, which must exercise an unfavourable effect.



(XXXIV.)



(XXXV.)

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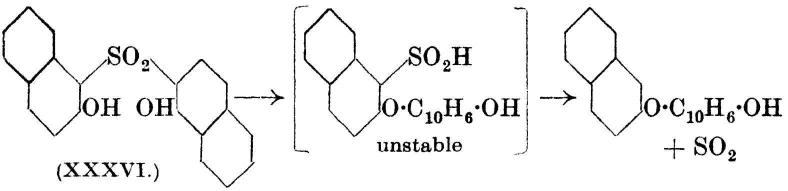
[59] A. W. Chapman and C. H. Perrott, *J.*, 1932, 1770; *A.*, 1932, 846.

[60] *Idem, J.*, 1930, 2462; *A.*, 1931, 87.

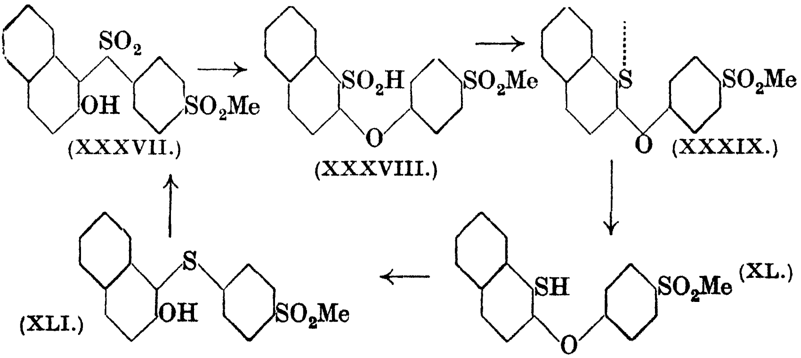
[61] L. A. Warren and S. Smiles, *J.*, 1931, 914; *A.*, 1931, 723.

Conversely, the change (in the absence of alkali) is accelerated by the addition of picryl chloride, although a picrate is not actually produced.

The reverse transformation, involving the migration of the aromatic residue from sulphur to oxygen, has also been realised,[62] starting from 2-naphthol-1-sulphone (XXXVI), in which the relative polarities of sulphur and oxygen are reversed; the naphthol residue therefore migrates to the more negative oxygen :



A number of other examples of this change have been observed [63, 64, 65] and the facts accord well with the authors' view of the process. Thus, the change is facilitated by the presence in the migrating group of a nitro-group,[63] which renders the carbon atom in the ortho-position strongly positive and facilitates attack by the phenolic ion at that point. Somewhat more drastic treatment is necessary to bring about the rearrangement of *o*-hydroxy-*p*-sulphonyl-sulphones. In one case it was possible to realise the complete cycle [64] from thiol oxide to hydroxy-sulphide and back : the sulphone (XXXVII) rearranges to the sulphinic acid (XXXVIII), which can be converted into the disulphide (XXXIX); this on reduction gives the thiol (XL), which rearranges to the sulphide (XLI), and this can be oxidised to the initial material, the sulphone (XXXVII) :



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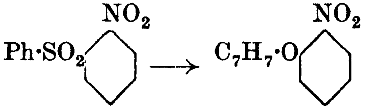
[62] L. A. Warren and S. Smiles, *J.*, 1931, 2207; *A.*, 1931, 1153.

[63] A. A. Levi, H. C. Rains, and S. Smiles, *ibid.*, p. 3264; *A.*, 1932, 156.

[64] L. A. Warren and S. Smiles, *J.*, 1932, 1040; *A.*, 1932, 735.

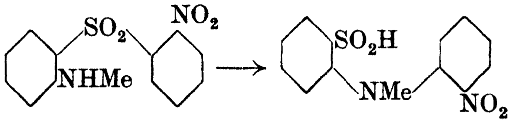
In the compound (XLII), the benzenesulphonyl group can be displaced by an intermolecular reaction, *e.g.*, by interaction with sodium *p*-tolyloxide :[65]

(XLII.)



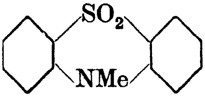
Moreover, *o*-amino-sulphones[66] and *o*-acetamido-sulphoxides[67] undergo the same rearrangement; for instance, the compound (XLIII) gives the sulphinate (XLIV) on treatment with alkali and this is further converted into the sulphone (XLV) with the loss of the nitro-group as nitrous acid :

(XLIII.)



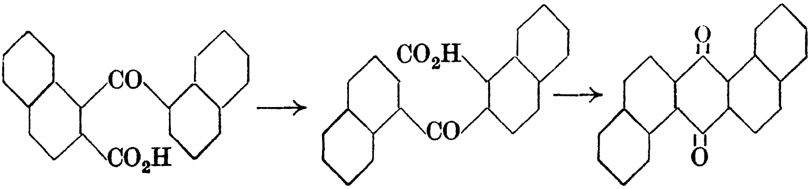
(XLIV.)

(XLV.)



$+ \mathrm{HNO_2}$

An entirely analogous change has also been observed in the similarly constituted ketones;[68] for example, the ketonic acid (XLVI) gives on dehydration 1 : 2 : 5 : 6-dibenzanthraquinone (XLVII) in place of the expected 1 : 2 : 7 : 8-compound.



(XLVI.) (XLVII.)

Proof is adduced that it is the naphthyl radical which undergoes migration and it is suggested that a similar mechanism accounts for the results recorded by M. Hayashi[69] in his study of substituted benzoylbenzoic acids. The migration of the aroyl residue is, however, also possible in compounds of this type, as in the following example : [70]

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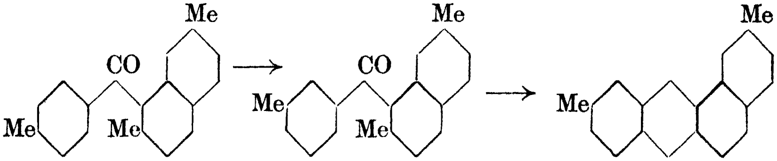
[65] A. A. Levi and S. Smiles, *J.*, 1932, 1488; *A.*, 1932, 735.

[66] L. A. Warren and S. Smiles, *ibid.*, p. 2774; *A.*, 1933, 58.

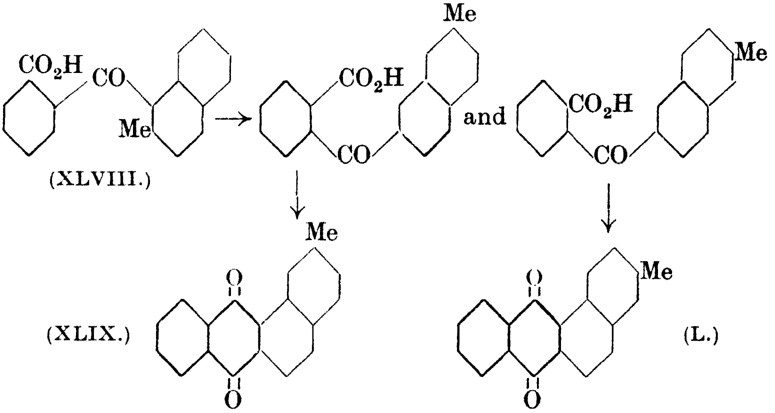
[67] A. A. Levi, L. A. Warren, and S. Smiles, *J.*, 1933, 1490.

[68] J. W. Cook, *J.*, 1932, 1472; *A.*, 1932, 747.

[69] *J.*, 1927, 2516; *A.*, 1927, 1197; *J.*, 1930, 1513, 1520, 1524; *A.*, 1930, 1183; compare *Ann. Reports*, 1930, **27**, 124.



Further cases of this rearrangement have been observed in the naphthoylbenzoic acids, in which a methyl group blocks ring formation. Thus, the acid (XLVIII) gives the two quinones (XLIX) and (L); the phthalyl residue here migrates from the α-position of the substituted ring to the β-position of the *unsubstituted* ring, a mechanism confirmed in a number of cases.[71]



(XLVIII.)

(XLIX.)

(L.)

In some instances a methyl group may also wander.[72]

Podophyllin.

It has long been known that the active principle of both Indian and American podophyllin, which is still extensively used as a purgative, is the lactone podophyllotoxin,[73] first obtained pure by Kürsten ; [74] he also recognised the isomeric lactone picropodophyllin and proved that three methoxyl groups are present in both compounds, which give, as Dunstan and Henry [73] showed, the same hydroxy-acid, podophyllic acid. The researches published in the last two years have elucidated the structure of these two compounds except for one or two minor points.

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[70] J. W. Cook, *J.*, 1932, 456; *A.*, 1932, 374; J. W. Cook and R. A. E. Galley, *J.*, 1931, 2012; J. W. Cook, *ibid.*, p. 487; *A.*, 1931, 1157, 612.

[71] L. F. Fieser and M. A. Peters, *J. Amer. Chem. Soc.*, 1932, **54**, 3742; *A.*, 1932, 1136.

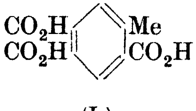
[72] L. F. and M. Fieser, *ibid.*, 1933, **55**, 3342; *A.*, 1053.

[73] W. R. Dunstan and T. A. Henry, *J.*, 1898, **73**, 209.

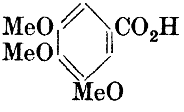
[74] *Arch. Pharm.*, 1891, **229**, 220; *A.*, 1891, i, 1133.

Podophyllotoxin, which crystallises with a variety of solvents of crystallisation, has the formula $C_{22}H_{22}O_8$.[75] Two non-phenolic hydroxyl groups appeared at first to be present, although the compound only yields a monoacetyl derivative; under more drastic conditions the acetyl derivative of picropodophyllin is produced. The latter acetyl compound loses acetic acid, giving the unsaturated *apo*picropodophyllin. The most important discovery, however, was the degradation of podophyllotoxin with hydriodic acid in acetic acid, to podophyllomeronic acid, $C_{13}H_{10}O_4$, a monocarboxylic acid which was thought to contain a hydroxyl group owing to the formation of an unstable acetyl compound, later recognised as a mixed anhydride; the new acid was oxidised to an acid, $C_7H_5(CO_2H)_3$.

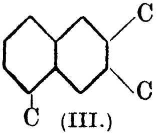
Later work [76] appeared to show that only one hydroxyl group was present in podophyllotoxin and picropodophyllin and none in phyllomeronic acid, and confirmed the suggestion that the isomeric lactones differ owing to the participation of different hydroxyl groups in lactonisation. The acid produced by the oxidation of phyllomeronic acid was oxidised to pyromellitic acid, and was thus proved to be toluene-2 : 4 : 5-tricarboxylic acid (I). Pyromellitic acid also resulted from the vigorous oxidation of phyllomeronic acid; and the important observation was made that both lactones give trimethylgallic acid (II) on oxidation with hot permanganate :



(I.)



(II.)



(III.)

By distillation with zinc dust a naphthalene hydrocarbon, erroneously identified as 1 : 6-dimethylnaphthalene, was obtained from both lactones, and the naphthalene-like arrangement of the molecule was expressed in the scheme (III). Since this accounts for 13 carbon atoms, and the trimethylgallic residue for 10 more, it is clear that one of these must be common to both residues, in other words the trimethylgallic residue must be directly attached to one carbon atom of the hydronaphthalene skeleton. This conclusion is correct, though based on false premises.

In a paper which appeared immediately afterwards, W. Borsche and J. Niemann [77] virtually settled the issue. They, too, identified the acid $C_7H_5(CO_2H)_3$ as toluenetricarboxylic acid and isolated trimethylgallic acid; in addition, by fusing podophyllomeronic acid (IV) with alkali, they obtained phyllomeronic acid, which contains two phenolic hydroxyl groups, and showed that these two acids are related in the same way as piperonylic and protocatechuic acid. Phyllomeronic acid (V) is decarboxylated to a phenol, phyllomerol (VI), and passes on distillation with zinc dust into 2-methylnaphthalene:

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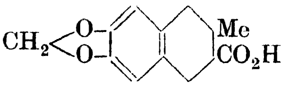
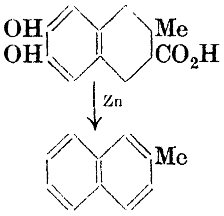
[75] W. Borsche and J. Niemann, *Annalen*, 1932, **494**, 126; *A.*, 1932, 618.

[76] E. Späth, F. Wessely, and L. Kornfeld, *Ber.*, 1932, **65**, [*B*], 1536; *A.*, 1932, 1137.

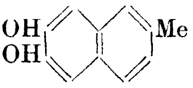
(IV.)





(V).

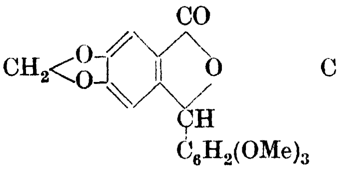
(VI.)

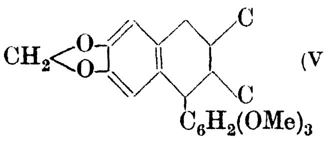


The attachment of the methylenedioxy-group to ring II follows because, as the carboxyl and the methyl group occupy the two β-positions (formation of toluene-2 : 4 : 5-tricarboxylic acid), there is no room for it in ring I; the actual position of the residue is based on purely theoretical considerations, subsequently shown to be justified (p. 195).

The position of the trimethylgallic residue is deduced from the oxidation of podophyllic acid to a lactone $C_{18}H_{16}O_7$, which is formulated as (VII), and the skeleton of the parent acid as (VIII):

(VII.)





(VIII.)

It is suggested that the free hydroxyl of picropodophyllin, resulting from the opening of the lactone ring of podophyllotoxin, must be in the γ-position to the carboxyl, but cannot be attached to the same carbon atom as the trimethylgallic residue, because the formation of the lactone (VII) would be difficult to interpret; the oxidation of podophyllic acid would then presumably attack this quaternary carbon atom. The hydroxyl is therefore placed on C_1, in good agreement with the ready formation of picropodophyllin from the acid. The following formulæ are suggested:

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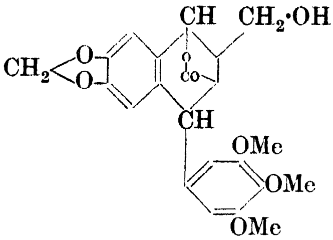
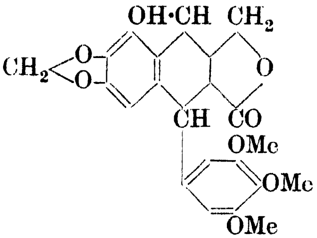
[77] *Annalen*, 1932, **499**, 59; *A.*, 1932, 1258.

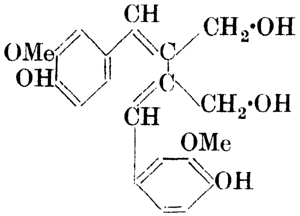


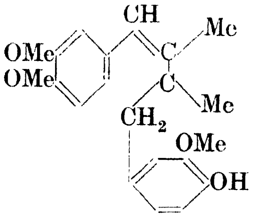
Podophyllotoxin.



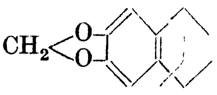
Picropodophyllin.

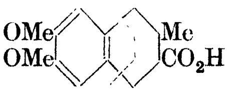
The formulæ show a distinct similarity to those of coniferyl alcohol and guajaretic acid : [78]



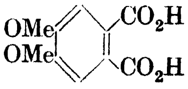


Identical conclusions were also reached by E. Späth, F. Wessely, and E. Nadler,[79] who obtained hydrastic acid by the oxidation of podophyllotoxin, thus confirming the position of the methylenedioxy-group; and phyllomeronic acid was methylated, and the product (IX) similarly oxidised to hemipinic acid :



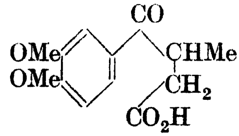


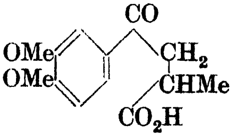
(IX.)



Phyllomerol and podophyllomerol have been synthesised by A. Robertson and R. B. Waters [80] by condensing veratrole with methylsuccinic anhydride to a mixture of the two ketonic acids (X) and (XI), which were reduced and cyclised to the corresponding tetralones (XII) and (XIII). These were reduced, and the product was dehydrogenated with selenium to phyllomerol dimethyl ether (XIV) :

(X.)





(XI.)

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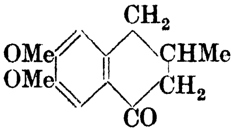
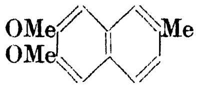
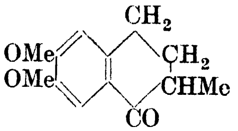
[78] G. Schroeter, L. Lichtenstadt, and D. Irineu, *Ber.*, 1919, **51**, 1587; *A.*, 1919, i, 84.

[79] *Ber.*, 1932, **65**, [*B*], 1773; *A.*, 73.

[80] *J.*, 1933, 83; *A.*, 277.


(XII.)

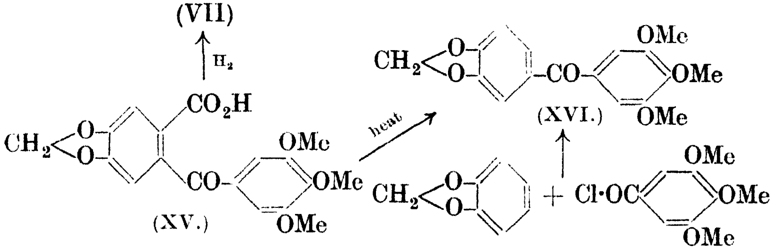

(XIV.)


(XIII.)

Phyllomerol itself could be obtained from this by demethylation, and podophyllomerol by subsequent treatment with sodium methoxide and methylene iodide.

Exactly the same synthesis was also carried out by Borsche and Niemann,[81] who, in addition, separated the two acids (X) and (XI) and prepared the latter by an alternative method. This synthesis proves the position of the methylenedioxy-group deduced by the authors, because this is the only arrangement which allows the formation of two *different* tetralones both giving the same final product.

The position of the trimethylgallic residue cannot be regarded as proved. Robertson and Waters place this on C_1, but this can hardly be reconciled with the formation of the lactone (VII). Additional evidence is provided by the oxidation of either podophyllotoxin or picropodophyllin to an acid $C_{18}H_{16}O_8$ (XV),[82] which is decarboxylated to the ketone (XVI); this has been synthesised from the chloride of trimethylgallic acid and pyrocatechol methylene ether. On reduction, the acid (XV) passes into Borsche and Niemann's lactone (VII):



The positions of the free hydroxyl group in podophyllotoxin and of that in picropodophyllin are also not proved in the strict sense, although those allocated are probably correct.

Auxins.

Although the interest of the phytohormones is mainly biological, sufficient insight has now been gained into their chemistry to justify a brief account.

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[81] *Annalen*, 1933, **502**, 264; *A.*, 709.

[82] E. Späth, F. Wessely, and E. Nadler, *Ber.*, 1933, **66**, [*B*], 125; *A.*, 278.

The presence of hormones responsible for the stretching of cells in young plant shoots has been known for some time and their action has been experimentally demonstrated;[83] it is connected with the phenomena of geotropism and phototropism—the bending of the shoots away from the ground and towards light.[84] The active substance is present in a variety of materials other than seedlings; the assay of it is possible with the aid of Went's test, the activity being expressed in Avena units (one unit produces a 10° bending of a seedling in Went's test).

Urine is by far the richest source of the hormone, which requires a 21,000 fold concentration for complete purification; it is estimated that the best vegetable source (maize seedlings) contains only 1/25 part of this amount.[85]

Auxin is extracted by a complicated process, which takes advantage of its acidic nature and the formation of sparingly soluble lead salts; it is finally esterified (more correctly, lactonised) and obtained crystalline by distillation in a high vacuum.

Although only a very small quantity of the pure material (some 350 mg.) has as yet been isolated, an astonishingly thorough chemical examination has been made. Auxin is a monobasic acid, $C_{18}H_{32}O_5$, containing three hydroxyl groups (formation of a trisdinitrobenzoyl derivative); it is accompanied by its equally active lactone, $C_{18}H_{30}O_4$, into which it can be converted by means of alcoholic hydrogen chloride.[86] It is feebly lævorotatory and exhibits mutarotation owing to lactone formation, equilibrium being reached in 1—2 hours: it is inferred from this that auxin must be a δ-hydroxy-acid, since γ-hydroxy-acids usually take much longer to reach equilibrium.[87] The physiological activity of auxin and its lactone disappears on keeping owing to isomerisation into an inactive pseudoauxin.

The molecule contains one double bond and is catalytically reduced to a physiologically inactive dihydro-compound, $C_{18}H_{34}O_5$; as this is saturated, it must contain a ring, since a straight-chain saturated compound would have the formula $C_{18}H_{36}O_5$.

Oxidation of either of the active compounds with alkaline permanganate leads to a dibasic acid, $C_{13}H_{24}O_4$, evidently by the rupture of the molecule at the double bond; the hydroxyl groups are no longer present in the new acid. If it is assumed that one of the carboxyls of the new acid is that present in the original compound, the hydroxyl group in the δ-position to it must be eliminated in this degradation, thus :[88]

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[83] For a detailed account and bibliography, see F. Kögl, A. J. Haagen-Smit, and H. Erxleben, *Z. physiol. Chem.*, 1933, **214**, 241; *A.*, 435.

[84] F. A. F. C. Went, *Naturwiss.*, 1933, **21**, 1.

[85] F. Kögl, *ibid.*, p. 17; *A.*, 435.

[86] F. Kögl, *loc. cit.*; F. Kögl, H. Erxleben, and A. J. Haagen-Smit, *Z. physiol. Chem.*, 1933, **216**, 31; *A.*, 612.

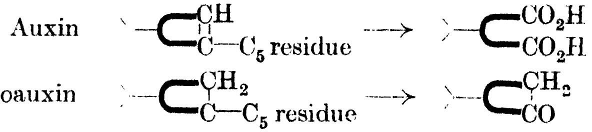
[87] W. N. Haworth, "The Constitution of the Carbohydrates," 1931.

$$R{\cdot}C(CO_2H){:}CH{\cdot}\overset{|}{C}{\cdot}C(OH){<} \longrightarrow R{\cdot}CO{\cdot}CO_2H$$

or $$R{\cdot}CH(CO_2H){\cdot}CH{:}\overset{|}{C}{\cdot}C(OH){<} \longrightarrow R{\cdot}CH(CO_2H)_2$$

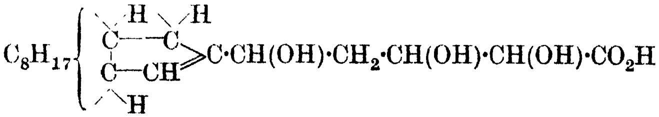
The C_{13}-acid is not a malonic acid and contains no keto-group. It is therefore assumed that the original carboxyl is eliminated as part of the C_5-residue, which must in that case carry all the hydroxyl groups, whilst two new carboxyls are formed by the opening of an unsaturated ring. Confirmation of this view has been obtained by the oxidation of dihydroauxin with chromic acid, a ketone $C_{13}H_{24}O$ being produced. Here again the C_5-residue has been eliminated, leaving a keto-group, but the ring, being saturated, has not been opened.

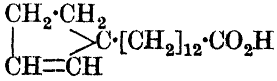
This can be represented as follows :



The C_{13}-acid forms an anhydride, not a cyclic ketone, on heating and is therefore a glutaric and not an adipic (or pimelic) acid, from which it can be inferred that the unsaturated ring of auxin is five-membered; moreover, the C_5-residue must be attached to one of the unsaturated carbon atoms, and the other must carry a hydrogen atom, to account for the formation of a dibasic acid on oxidation.

As regards the C_5-residue, it appears highly probable that there is no hydroxyl attached to the γ-carbon atom, since γ-hydroxy-acids lactonise with great ease, whereas auxin is stable ; there must therefore be hydroxyls in the α- and β-positions. These facts can be expressed in the following scheme :





Chaulmoogric acid (also represented above) contains 18 carbon atoms and an unsaturated *cyclo*pentane ring ; the latter is, however, at the end of the molecule.

[88] F. Kögl, *Angew. Chem.*, 1933, **46**, 469 ; *A.*, 987.

The principal problem remaining to be solved is the nature and point of attachment of the remaining 8 carbon atoms, and this may well be settled by the synthesis of the appropriate C_{13} glutaric acid, even though there are, as Kögl points out, some 1200 possible isomerides.

Auxin obtained from vegetable sources [89] contains, in addition to auxin A identical with the compound isolated from urine, a second physiologically active, acidic substance auxin B, isomeric with auxin lactone and containing a keto-group in addition to a hydroxyl; the latter is probably in the δ-position to the carboxyl, just as in auxin A. Auxin B loses carbon dioxide on melting and is formulated as a β-ketonic acid: $R{\cdot}CH(OH){\cdot}CH_2{\cdot}CO{\cdot}CH_2{\cdot}CO_2H$. It is therefore probably related to auxin A in the same way as œstrone to œstriol (p. 216). A transition from auxin B to auxin A has not yet been achieved, but they must contain the same carbon skeleton, because the same C_{13}-acid has also been obtained from auxin B.

As auxin B is present in the diet but is not excreted, it is probably converted into auxin A in the course of metabolism. The excretion of auxin A reaches a maximum 2 hours after the principal meal and a definite connexion has been traced between fats—especially vegetable oils—and the output of auxin; this appears to be present in vegetable oils in the form of ester.

Of the many interesting biological observations which have already accumulated in connexion with these substances, one fact cannot fail to be significant: the absorption of auxin is dependent on the electrical condition of the atmosphere and can be greatly increased by passing a weak electric current (0·0008 milliamp. and a potential difference of 80 millivolts/cm.), with the negative pole connected to the point at which the auxin is applied to the plant, and the positive pole to the containing vessel; conversely, the activity diminishes to 1/12 on reversal of the current.

Sterols and Bile Acids.

(Continued from *Ann. Reports*, 1931, **28**, 139.)

The two years under review have seen a vast output of work on this subject [90] and it can be said that the main structural outlines of this important group are now settled.

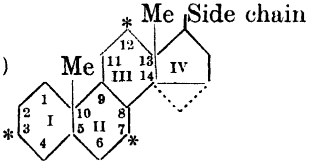
The stimulus which led to this development was the new formula

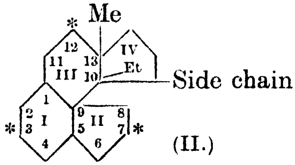
[89] F. Kögl, *loc. cit.*; F. Kögl, H. Erxleben, and A. J. Haagen-Smit, *Z. physiol. Chem.*, 1933, **220**, 137; F. Kögl, A. J. Haagen-Smit, and B. Tönnis, *ibid.*, p. 162; *A.*, 1213.

[90] For a summary of the present position, see I. M. Heilbron, J. C. E. Simpson, and F. S. Spring, *J.*, 1933, 626; also A. Windaus, *Z. physiol. Chem.*, 1932, **213**, 147.

(I) proposed for the sterols and bile acids by O. Rosenheim and H. King.[91]

(I.)





(II.)

* Position of OH groups.

The inadequacy of such formulæ as (II) was becoming increasingly apparent in the last few years and numerous variants of them were put forward without much success; [92] finally, the *X*-ray measurements of J. D. Bernal [93] showed that none of them could be correct, because the space occupied by a molecule in which one carbon atom is common to three rings (C_9 in II) would be far greater than that actually observed; the measurements indicated a flat molecule, with a condensed ring system such as (I) and, in addition, a different position of the side chain from that formerly adopted.

Rosenheim and King originally based their formula on the production of chrysene by the dehydrogenation of several compounds of this group by Diels and his collaborators,[94] and their first formula (marked by a dotted line in I) was that of a hydrochrysene; shortly afterwards [95] they admitted the possibility of ring IV being five-membered, a formulation also independently suggested by H. Wieland and E. Dane [96] and universally accepted. The workers of the German school have since contributed most of the additional evidence, which has removed the discrepancies arising out of the new formulation and will now be briefly reviewed.

The five-membered nature of ring II in the old formula rested on the fact that a dibasic acid, $C_{27}H_{46}O_4$, obtained by the opening of this ring yields an anhydride and not a ketone on pyrolysis (Blanc's rule). O. Stange [97] has since obtained such a ketone by pyrolysis of the barium salt of this acid, and has thus removed all doubts as to the six-membered structure of this ring. Similarly,[96] the acid (III) (thilobilianic acid), obtained by opening ring III of the old formula for 12-hydroxycholanic acid, also does not give a ketone on pyrolysis and it is concluded that Blanc's rule only applies when

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[91] *Chem. and Ind.*, 1932, **51**, 464, 954; *A.*, 1932, 736; 1933, 62.

[92] These difficulties are summarised by Heilbron and collaborators (ref. 90).

[93] *Chem. and Ind.*, 1932, **51**, 466; *A.*, 1932, 736.

[94] See *Ann. Reports*, 1927, **24**, 146.

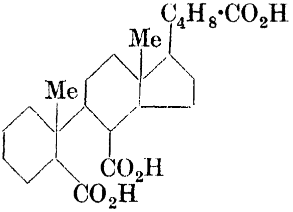
[95] *Nature*, 1932, **130**, 513; *A.*, 1932, 1131.

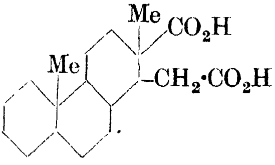
[96] *Z. physiol. Chem.*, 1932, **210**, 268; *A.*, 1932, 1131.

[97] *Ibid.*, 1933, **218**, 74; *A.*, 1047.

both carboxylated side chains are attached to the same ring; the evidence at the same time disposes of the possibility of ring III being seven-membered.

(III.)

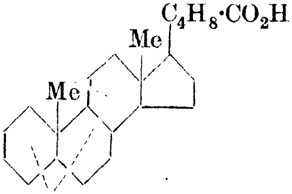




(IV.)

On the other hand, ætiobilianic acid (IV), which is similarly produced by the fission of ring IV and also does not give a ketone, is considered to be a glutaric acid because both residues are attached to the same ring and Blanc's rule would therefore be expected to hold. For this reason the five-membered ring IV is retained by Wieland and Dane.

If ring IV is five-membered, one carbon atom remains to be accommodated and this is placed in the form of a methyl group in position 10.[96] This is necessary to account for the formation of α-carboxy-α-methylglutaric acid, which can no longer represent the methyl-bearing carbon atom 13 (as in the old formula) owing to the presence of the side chain attached to the adjoining carbon atom :



Evidence for this is forthcoming from the work of R. Tschesche,[98] who suggests that C_{10} is probably quaternary owing to the difficulty experienced in esterifying a carboxyl group attached to it.*

More important, however, is the proof contained in the same paper, that position I is occupied by a methylene group, which is incompatible with the old formulation, since the carbon atom in question was represented as shared between two rings. The starting point of the research is the acid $C_{26}H_{44}O_3$ originally obtained[99] by the oxidation of cholestenone, at that time assumed to be a Δ^{β}-unsaturated ketone. Recent measurements of absorption spectra show, however, that cholestenone must be unsaturated in the αβ-position,[1] and still later work shows that it is the ketone corresponding to *allo*cholesterol, not cholesterol itself.[2] The oxidation of cholestenone can be readily interpreted if it be assumed that the keto-group, and therefore the hydroxyl of cholesterol, is in position 3, not 4 as formerly believed (that is, in the same position as one of the hydroxyls in the bile acids; compare p. 204):

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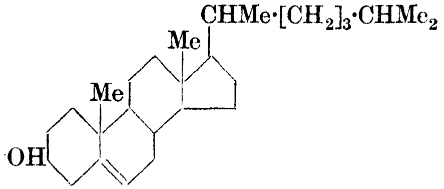
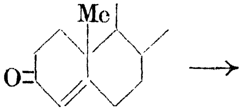
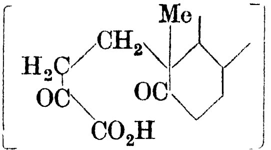
[98] *Annalen*, 1932, **498**, 185; *A.*, 1932, 1131.
[99] A. Windaus, *Ber.*, 1917, **50**, 133; *A.*, 1917, i, 265.
* See also p. 203.



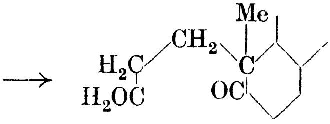
Cholesterol (V.)



Cholestenone (VI.)

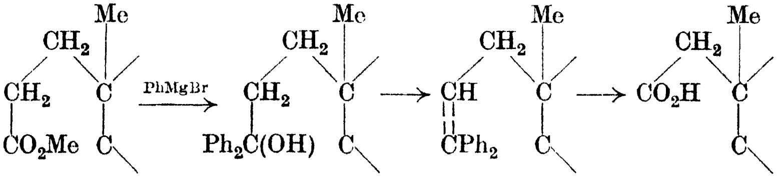


Ketonic acid (VII.)



Windaus's acid $C_{26}H_{44}O_3$ (VIII.)

The acid $C_{26}H_{44}O_3$ was reduced by Clemmensen's method, the new acid esterified, and the ester treated with phenylmagnesium bromide; the product on dehydration gave a hydrocarbon, which by the action of ozone, followed by chromic acid, gave the lower homologue of Windaus's acid:



Acid $C_{25}H_{42}O_3$.

Tscheche was able to repeat the shortening of the chain once again, thus proving that the carboxyl group in the original acid must have been attached to a chain of not less than two methylene groups.

One of the most serious difficulties in explaining the degradations of the bile acids on the basis of the new formulæ lay in the supposed proof that the second hydroxylated ring of deoxycholic acid (ring II of the old formula) was identical with the unsaturated ring II of cholesterol.[3] By the opening of both hydroxylated rings of deoxycholic acid, an acid (choloidanic acid) was produced, which behaved as an adipic *and* a glutaric acid, giving on pyrolysis the anhydride of a ketonic acid; it was therefore assumed that, in addition to the six-membered ring I, a five-membered ring had been opened, identical with the supposedly five-membered ring II of cholesterol. The further degradation of pyrocholoidanic acid (compare *Ann. Reports*, 1927, **24**, 137) could not be interpreted unless it was assumed that this ring had two carbon atoms in common with ring I. We now know that Blanc's rule does not hold in such cases and that this ring can be six-membered; and the behaviour of choloidanic acid is explained in a simple manner when it is realised that the second ring opened in deoxycholic acid is, in effect, ring III:[4]

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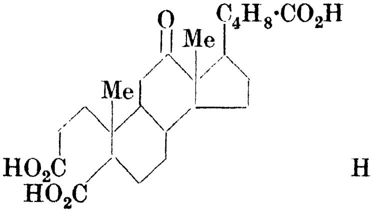
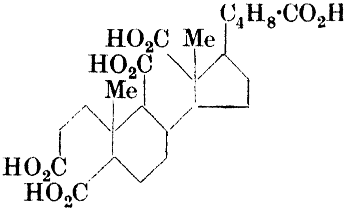
[1] W. Menschick, I. H. Page, and K. Bossert, *Annalen*, 1932, **495**, 225; *A.*, 1932, 746.

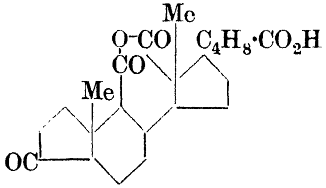
[2] K. Bonstedt, *Z. physiol. Chem.*, 1933, **214**, 173; *A.*, 390.



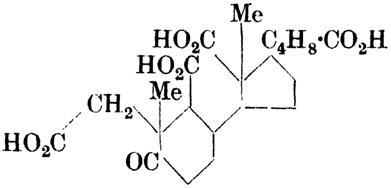
Deoxybilianic acid (IX.)



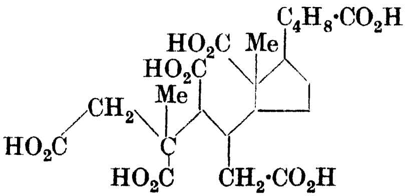
Choloidanic acid (X.)



Pyrocholoidanic acid (XI.)*



Prosolannellic acid (XII.)



Solannellic acid (XIII.)

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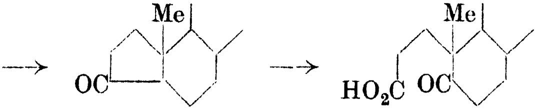
[3] H. Wieland and W. Schulenburg, *Z. physiol. Chem.*, 1921, **114**, 167; *A.*, 1922, i, 346.

[4] H. Wieland, E. Dane, and W. Schönberger, *ibid.*, 1932, **211**, 177; *A.*, 1932, 1248.

* Pyrocholoidanic acid is an enolic lactone, probably formed by the interaction of the carboxyl on C_{13} with the keto-group; this does not affect the argument developed here.

An acid analogous to prosolannellic acid but still containing ring III intact has been obtained by a similar process, the oxidation of deoxybilianic acid itself, however, being omitted, thus :

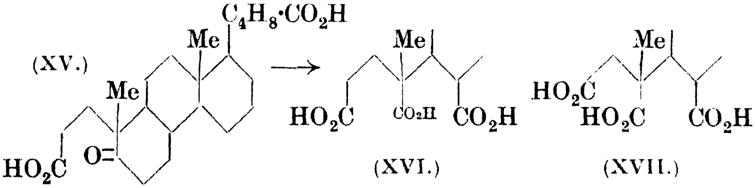
(IX)



(XIV.)

The further oxidation of the acid (XIV) leads to the opening of two rings, II and III. In order to avoid this, the same sequence of operations has been repeated starting with lithocholic acid, which has no hydroxyl other than that in ring I. The degradation of this acid [5] through the corresponding bilianic acid leads to a ketonic acid (XV) which must have the carbonyl group in a ring condensed with ring I. This ring is now opened by oxidation, and the shortening of the resulting carboxylated chains completed by pyrolysis and oxidation in the usual way :

(XV.)



(XVI.) (XVII.)

The acids (XVI) and (XVII) were found to be identical with two acids previously obtained by the vigorous oxidation of the tricarboxylic acids $C_{25}H_{42}O_6$ and $C_{24}H_{40}O_6$ resulting from the opening of rings I and II of cholesterol.[6] Now Windaus has found that his C_{24}-acid, which is converted into (XVII) by oxidation of the *iso*propyl group to carboxyl, once more undergoes cyclisation and on opening of the new ring gives a malonic acid ; this loses a carboxyl when heated but no longer undergoes cyclisation. To account for this it is necessary to assume that one carbon atom is present in the form of a methyl group attached to C_{10},[7] since otherwise the acid would be expected to form a ketone. It is also clear that this sequence of degradations is only possible if ring II of cholesterol is six-membered.

As already pointed out, the oxidation of lithocholic acid leads to the opening of the ring formerly described as III (identical with the oxygen-free ring of deoxycholic acid); the identity of this ring with ring II of cholesterol is therefore established.

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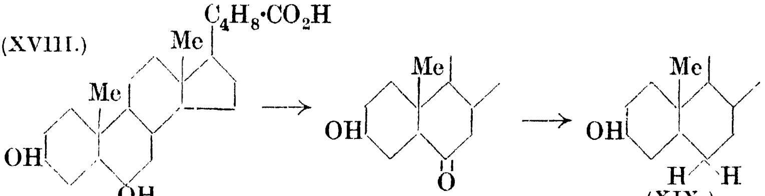
[5] H. Wieland, E. Dane, and E. Scholz, *Z. physiol. Chem.*, 1932, **211**, 261 ; *A.*, 1932, 1245.

[6] *Ber.*, 1908, **41**, 611 ; *A.*, 1908, i, 264 ; *ibid.*, 1912, **45**, 1316 ; *A.*, 1922, i, 449.

[7] H. Wieland and E. Dane, *Z. physiol. Chem.*, 1933, **216**, 91 ; *A.*, 609.

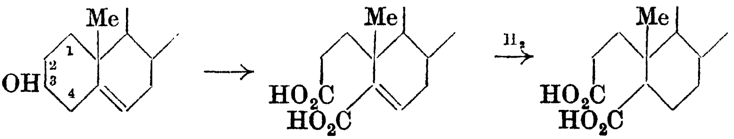
As a consequence of this a number of bile acids have to be renamed: deoxycholic, chenodeoxycholic, and hyodeoxycholic acid become 3 : 12-, 3 : 7-, and 3 : 6-dihydroxycholanic acid, respectively; cholic acid, which has a hydroxyl in each of the first three rings, remains unchanged.[8]

The important assumption that the hydroxyl of the sterols occupies the same position as one of the hydroxyls of the bile acids (p. 201) has been confirmed by experiment;[9] hyodeoxycholic acid (XVIII) has been converted, through the 3-hydroxy-6-keto-acid, into a stereoisomeride of lithocholic acid, *allo*-lithocholic acid (XIX), which has since been found identical[10] with an acid obtained by the oxidation of chlorocholestane and replacement of chlorine by hydroxyl:[11]



(XVIII.) (XIX.)

The formulæ allotted to deoxybilianic and *iso*deoxybilianic acid (and other similar pairs of acids) have been interchanged,[12] the opening of ring I in the normal series being represented as taking place between C_3 and C_4 and not symmetrically (between C_2 and C_3). Experimental support for this will be found in the work summarised on p. 203. The acid $C_{25}H_{42}O_6$ was originally obtained by the oxidation of Diels's acid (XX), resulting from the opening of ring I of cholesterol by hypobromite:



(XX.) (XXI.)

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[8] H. Wieland and E. Dane, *Z. physiol. Chem.*, 1932, **210**, 268; *A.*, 1932, 1131.

[9] *Idem, ibid.*, 1932, **212**, 41; *A.*, 64.

[10] H. Wieland, private communication; H. Wieland, E. Dane, and C. Martius, *Z. physiol. Chem.*, 1933, **215**, 15; *A.*, 504.

[11] A. Windaus and R. Hossfeld, *ibid.*, 1925, **145**, 177; *A.*, 1925, 1066.

[12] H. Wieland, E. Dane, and L. Maiweg, *ibid.*, 1932, **211**, 164; *A.*, 1932, 1248.

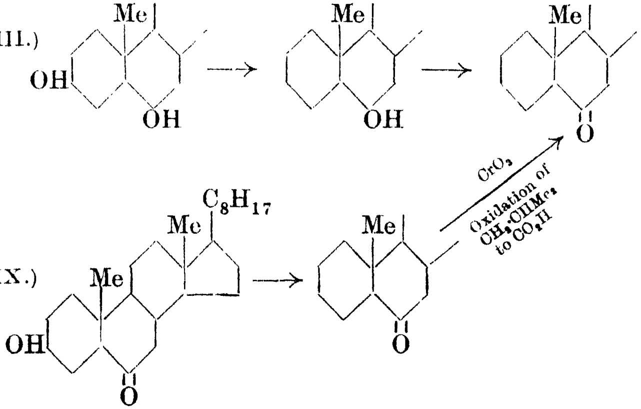
The opening of the ring must, as we have already seen, lead to the formation of a propionic-acid chain to enable the subsequent degradations of the acid to be formulated.

Now Diels's acid can be hydrogenated to an acid (XXI) stereoisomeric with the acid produced by the oxidation of coprosterol; this acid had been converted, by oxidation of the *iso*propyl group of the side chain of the sterol, into a bile acid derivative, *iso*-lithobilianic acid.[13] It could thus be inferred that this compound, like Diels's acid and the acid from coprosterol, must have a propionic-acid chain. When this work was repeated with pure materials, the sole product was lithobilianic acid.[14]

The interesting observation has also been made [15] that compounds of the *allo*-series (cholestanol and 3-hydroxy-*allo*cholanic acid) give acids of the bilianic acid type by the opening of the ring between C_3 and C_4, whereas their stereoisomerides yield mainly the symmetrical compounds.

The two hydroxyls of hyodeoxycholic acid (XVIII) have been proved to be in the 1 : 4-position to each other and to be situated in adjoining rings with two or more carbon atoms in common,[16] and the same has also been demonstrated for the hydroxyl and the keto-group of cholestanonol (XX).[17] These two compounds have now been converted into the same 6-keto-*allo*cholanic acid (XXI) : [18]

(XVIII.) (XXI.) (XX.)



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[13] A. Windaus and H. Riemann, *Z. physiol. Chem.*, 1923, **126**, 277; *A.*, 1923, i, 567.

[14] R. Langer, *ibid.*, 1933, **216**, 189; *A.*, 710.

[15] H. Wieland, E. Dane, and C. Martius, *ibid.*, **215**, 15; *A.*, 504.

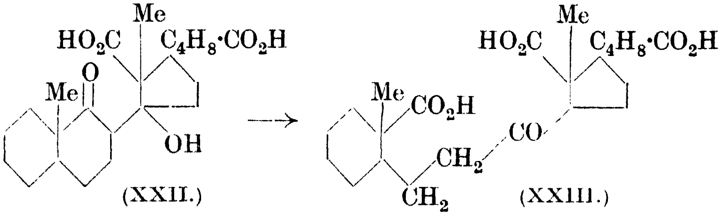
[16] A. Windaus, *Annalen*, 1926, **447**, 233; *A.*, 1926, 723.

[17] *Idem*, *Ber.*, 1903, **36**, 3752; 1906, **39**, 2249; compare *Ann. Reports*, 1927, **24**, 131.

[18] O. Stange, *Z. physiol. Chem.*, 1933, **220**, 34; *A.*, 1162; compare also H. Lettré, *ibid.*, **221**, 73.

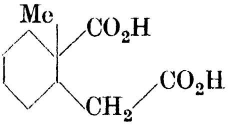
This proves once more the identity of ring II of cholesterol with ring III of the old bile acid formula and also serves to establish the position assigned to the double bond of this sterol.

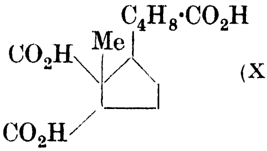
Additional information regarding ring IV has been obtained as follows: the ketonic acid (XXII)[19] was brominated, the bromine replaced by hydroxyl, and ring II opened by oxidation; the acid (XXIII) was one of the products.[20]



(XXII.) (XXIII.)

(XXIV.)





(XXV.)

On further oxidation, (XXIII) gave the well-known acid $C_{13}H_{20}O_6$ (XXV); the other fragment (XXIV), which might have been expected, was not isolated.

The acid (XXV) is a *trans*-acid, but is convertible into the anhydride of the *cis*-form. Since this acid is also produced by the oxidative fission of a pyro-acid derived from the acid $C_{16}H_{24}O_8$,[21] it can be argued that the latter must have contained the appropriate carboxyl groups already in the *trans*-position and that therefore rings III and IV are fused in the *trans*-position. This also explains the poor yield of the pyro-acid.

The inability of the *trans*-C_{16}-acid to pass into the *cis*-ketone on pyrolysis must be due to the carboxyl being attached to a quaternary carbon atom, namely, C_{13}; otherwise a change to the strain-free *cis*-form would be expected, just as in the analogous formation of α-hexahydrohydrindone. This can therefore be taken as an argument against the six-membered structure of ring IV, since no methyl group would in this case be present; it is also used as an argument for the attachment of the methyl to C_{13} and not C_{14}, otherwise the pyro-acid could be formed *with* change of configuration:

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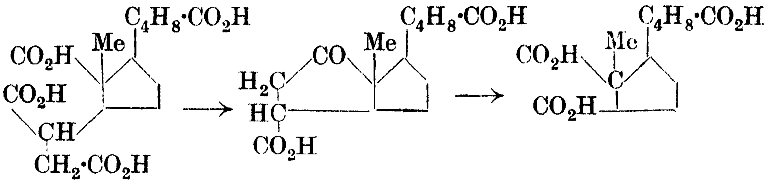
[19] H. Wieland and T. Posternak, *Z. physiol. Chem.*, 1931, **197**, 17; *A.*, 1931, 841.

[20] H. Wieland and E. Dane, *ibid.*, 1933, **216**, 91; *A.*, 609.

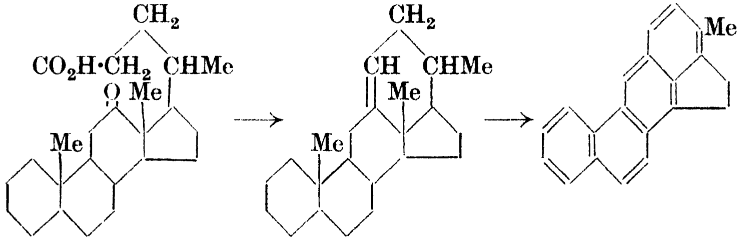
[21] H. Wieland, O. Schlichting, and R. Jacobi, *ibid.*, 1926, **161**, 80; *A.*, 1927, 247.



$C_{16}H_{24}O_8$. Pyro-acid. $C_{13}H_{20}O_6$. (XXV.)

Admittedly, such an argument does not amount to proof, as already pointed out by L. Ruzicka [22] in his review of the evidence; there is, however, a strong case in favour of the formulation adopted.

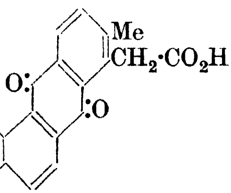
There is also no *proof* of the attachment of the side chain to C_{17}, but the following observations render it very probable: the pyrolysis of 12-ketocholanic acid (XXVI) leads to a hydrocarbon termed dehydronorcholene (XXVII); [23] this has lately been dehydrogenated to an aromatic hydrocarbon,[24] which has the structure (XXVIII), and the formation of which is difficult to explain in any other way than the following:

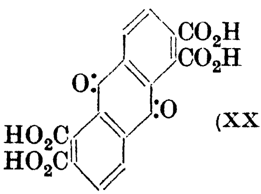


(XXVI.) (XXVII.) (XXVIII.)

The structure of the hydrocarbon (XXVIII) has been confirmed by its oxidation, first to the quinone carboxylic acid (XXIX) and finally to the known tetracarboxylic acid (XXX): [25]

(XXIX.)





(XXX.)

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[22] L. Ruzicka, M. W. Goldberg, and G. Thomann, *Helv. Chim. Acta*, 1933, **16**, 812; L. Ruzicka and G. Thomann, *ibid.*, p. 216; *A.*, 820, 278.

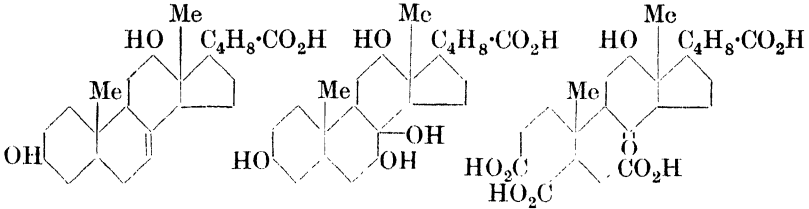
[23] H. Wieland and V. Wiedersheim, *Z. physiol. Chem.*, 1930, 186, 229; *A.*, 1930, 473.

[24] H. Wieland and E. Dane, *ibid.*, 1933, **219**, 240; *A.*, 1161.

[25] J. W. Cook and G. A. D. Haslewood, *Chem. and Ind.*, 1933, **52**, 758; J. W. Cook, C. L. Hewett, and G. A. D. Haslewood, *ibid.*, p. 949; *A.*, 1162.

The structures of *apo*cholic acid and its isomeride, 3 : 12 (formerly 3 : 7)-dihydroxycholenic acid, still present difficulties, well exemplified by the number of formulæ suggested by different workers.

The 3 : 12-dihydroxy-acid is oxidised by permanganate to a tetrahydroxy-acid which resists further attack; it was therefore concluded that the double bond is situated between two tertiary carbon atoms.[26] Later work [27] showed, however, that the acid can be oxidised by chromic acid, finally giving a ketonic acid $C_{24}H_{34}O_{10}$:



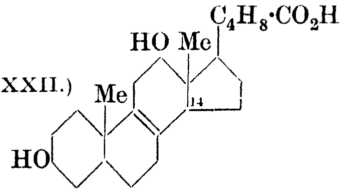
(XXXI.)

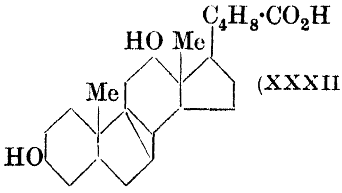
Acid $C_{24}H_{34}O_{10}$.

The structure of *apo*cholic acid is discussed in the same paper and it is suggested that, as the acid gives a colour with tetranitromethane and reacts with bromine and permanganate, it must contain a double bond, which is placed in position 8 : 9 (XXXII) (or 8 : 14) to account for its inert character. It is pointed out in support of this view that the dehydration of α-decalol leads to $\Delta^{9:10}$-octalin.[28] The catalytic reduction of *apo*cholatrienic acid goes no further than *apo*cholenic acid, which also has the inert "*apo*cholic" double bond; an analogy for such incomplete reduction is found in the hydrogenation of chrysene,[29] which also stops when a compound with a double bond between two rings is produced.

It seems to the Reporter that there is as much evidence in favour of the bridged formulation (XXXIII) for *apo*cholic acid suggested by O. Rosenheim and H. King; [30] such a formulation would account

(XXXII.)





(XXXIII.)

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[26] H. Wieland and E. Dane, *Z. physiol. Chem.*, 1932, **206**, 243; *A.*, 1932, 614.

[27] *Idem, ibid.*, 1932, **212**, 263; *A.*, 158.

[28] W. Hückel, R. Danneel, A. Schwartz, and A. Gercke, *Annalen*, 1929, **474**, 123; *A.*, 1930, 76.

[29] J. von Braun and G. Irmisch, *Ber.*, 1932, **65**, [*B*], 883; *A.*, 1932, 730.

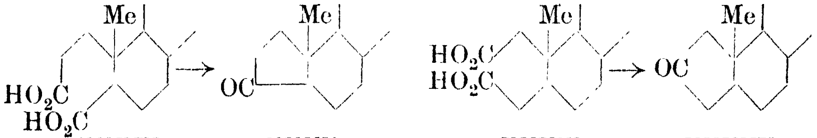
[30] *Chem. and Ind.*, 1932, **51**, 954; *A.*, 1933, 62

not only for the inert character of the double bond but also for the conversion of the acid into 3 : 12-dihydroxycholenic acid by the action of hydrochloric acid.

A second " *iso* "-dihydroxycholenic acid has lately been prepared by the action of hydrochloric acid on *apo*cholic acid;[31] the double bond in this is presumably in the position 8 : 14.

Some mention must be made of the stereochemistry of the cholane group. The flat molecule which is characteristic of them necessitates the *trans*-fusion of the two middle rings, for, as is seen on models, a flat structure results from the fusion of several *cyclo*hexane rings in the *cis*-position if the rings are fused linearly; with angular fusion, a *trans*-position gives a flat molecule.[32]

Now rings I and II can be fused in two ways and examples of both occur in nature. Windaus[33] has suggested that cholestane is the *trans*- and pseudocholestane the *cis*-form on the ground that cyclisation of lithobilianic and *allo*lithobilianic acid (XXXIV) produces the *same* α-ketone (XXXV), whereas different β-ketones result from *iso*lithobilianic and stadenic acid (XXXVI) :



(XXXIV.) (XXXV.) (XXXVI.) (XXXVII.)

The latter case is thus analogous to the formation of stable *cis*- and *trans*-β-decalones. Windaus assumed that the stable form of the α-ketone would be the *cis*; and as this on reduction gives the same hydrocarbon as the ketone (XXXVII) from *iso*lithobilianic acid, he concluded that the latter and lithobilianic acid are the *cis*-compounds. They are known to belong to the pseudocholestane group, whilst *allo*lithobilianic and stadenic acid, which must be the two *trans*-compounds, belong to the cholestane group.

These theoretical conclusions have now been confirmed by refractometric measurements[34] on cholestane and pseudocholestane and by a comparison of the melting points of different derivatives with those in the decalin series. The following configurations are suggested :

Cholestane, ***trans-trans-cis*** or ***trans-trans-trans***. Pseudocholestane, ***cis-trans-cis*** or ***cis-trans-trans***.

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[31] K. Yamasaki, *Z. physiol. Chem.*, 1933, **220**, 42; *A.*, 1162.

[32] L. Ruzicka and G. Thomann, *Helv. Chim. Acta*, 1933, **16**, 216; *A.*, 278.

[33] A. Windaus, *Annalen*, 1926, **447**, 233; *A.*, 1926, 723.

[34] L. Ruzicka, M. Furter, and G. Thomann, *Helv. Chim. Acta*, 1933, **16**, 327; *A.*, 495.

Finally, the evidence discussed on p. 206 makes the *trans*-fusion of rings III and IV highly probable, at any rate in cholesterol and the bile acids.

It is also pointed out [34] that the *trans*-fusion of rings II and III may easily account for the difficult formation (or non-formation) of ketones from 1 : 6-dicarboxylic acids obtained by the opening of ring II or III.

The configurations assigned to cholestane and pseudocholestane receive further support from the work of H. Lettré.[35]

Ergosterol.—Notwithstanding the great importance of this compound and the consequent wealth of research devoted to it, its constitution still presents difficulties. Indeed, it is only lately that the identity of its skeleton with that of other cholane derivatives has been finally demonstrated by the conversion of ergostane, the fully saturated parent hydrocarbon, into *allo*norcholanic acid by vigorous oxidation.[36] The hydroxyl must be situated in ring I, because the acid obtained by opening of the hydroxylated ring is readily cyclised to a ketone,[37] but its position is uncertain; since the oxidation of chloroergostane yields a chloro*allo*norcholanic acid different from that obtained from chlorocholestane, the position of the chlorine (and hence of the hydroxyls in the original sterols) must be different, unless the two acids are epimeric.[38]

The aldehyde previously obtained from the ozonide of ergosterol has been identified as methyl*iso*propylacetaldehyde,[39] and the same aldehyde has also been obtained from ergosterols B_1 and B_2, lumisterol, calciferol, and suprasterols I and II.[40] All these compounds therefore contain the same side chain $CHMe_2{\cdot}CHMe{\cdot}CH{:}CH{\cdot}CHMe^-$, and this is also present in the maleic anhydride addition products of ergosterol, dehydroergosterol, and tachysterol, showing that the conjugated double bonds in these compounds are independent of the double bond between C_{22} and C_{23} in the side chain; this double bond is not reduced by sodium and alcohol, but can be catalytically hydrogenated (giving α-ergostenol).

α-Ergostenol gives on oxidation with chromic acid an optically active ketone, formulated as dihydrothujaketone,[41]

$$CHMe_2{\cdot}CHMe{\cdot}CH_2{\cdot}CH_2{\cdot}COMe\,;$$

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[35] *Z. physiol. Chem.*, 1933, **221**, 73.

[36] C. K. Chuang, *Annalen*, 1933, **500**, 270; *A.*, 391.

[37] F. Reindel, *ibid.*, 1928, **466**, 131; *A.*, 1929, 61.

[38] I. M. Heilbron, K. M. Samant, and J. C. E. Simpson, *J.*, 1933, 1410; *A.*, 1290.

[39] F. Reindel and H. Kipphan, *Annalen*, 1932, **493**, 181; *A.*, 1932, 267.

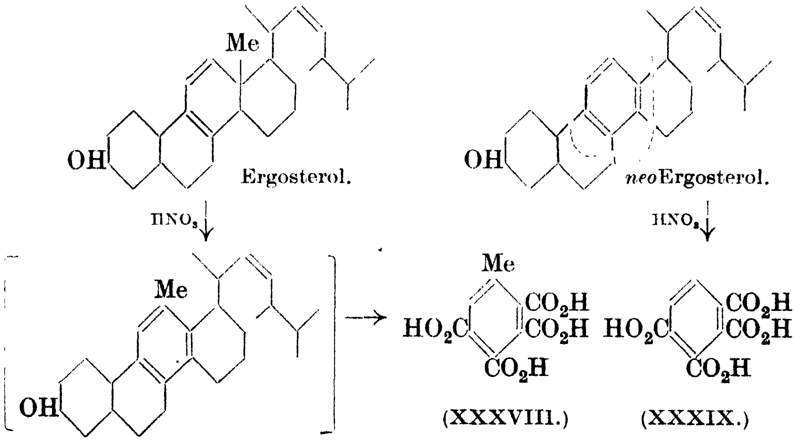
[40] A. Guiteras, Z. Nakamiya, and H. H. Inhoffen, *ibid.*, **494**, 116; *A.*, 1932, 611; compare I. M. Heilbron, J. C. E. Simpson, and D. G. Wilkinson, *J.*, 1932, 1699; *A.*, 1932, 485.

[41] A. Windaus, F. von Werder, and B. Gschaider, *Ber.*, 1932, **65**, [*B*], 1006; *A.*, 1932, 844.

the side chain therefore contains one carbon atom more than that of cholesterol. This discovery is in agreement with the recent analyses of ergosterol and its derivatives,[42] which suggest that ergosterol has the formula $C_{28}H_{44}O$, not $C_{27}H_{42}O$ as previously supposed, and lends support to the view that all the sterols have the same skeleton but differ in the nature of the side chains; stigmasterol has lately been found to give ethyl*iso*propylacetaldehyde on ozonisation, in agreement with the formula $C_{29}H_{46}O$ assigned to it.[43]

Oxidation of ergosterol, lumisterol, and dehydroergosterol with nitric acid gives rise to the same acid, previously thought to be $C_8H_6O_6$ [44] but now proved to be toluene-2 : 3 : 4 : 5 (or 2 : 3 : 5 : 6)-tetracarboxylic acid (XXXVIII); these compounds therefore probably contain a six-membered ring with two double bonds, and this becomes benzenoid on oxidation.

Ergosterol gives a bimolecular pinacol, ergopinacol,[45] $C_{56}H_{86}O_2$, which gives the characteristic colour reactions of ergosterol and is oxidised to the same acid.[46] It can be converted into *neo*ergosterol, which was thought to be isomeric with ergosterol but has now been shown to have the formula $C_{27}H_{40}O$ and to be formed with the loss of a methyl group in the form of methane, which was isolated. The new sterol was oxidised to benzene-1 : 2 : 3 : 4-tetracarboxylic acid (XXXIX). These changes are formulated as follows :



(XXXVIII.) (XXXIX.)

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[42] A. Windaus and A. Lüttringhaus, *Nach. Ges. Wiss. Göttingen*, 1932, 4.

[43] A. Guiteras, *Z. physiol. Chem.*, 1933, **214**, 89; *A.*, 271.

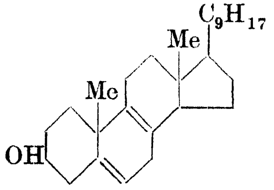
[44] F. Reinde and K. Niederländer, *Annalen*, 1930, **482**, 264; *A.*, 1930, 1578.

[45] A. Windaus and P. Borgeaud, *ibid.*, 1928, **460**, 235; *A.*, 1928, 425; K. Bonstedt, *Z. physiol. Chem.*, 1929, **185**, 165; *A.*, 1930, 84.

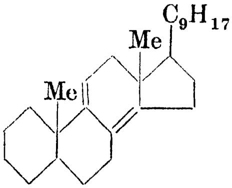
[46] H. H. Inhoffen, *Annalen*, 1932, **497**, 130; *A.*, 1932, 944.

The oxidation of ergosterol is therefore assumed to involve the migration of a methyl group, which evidently prevents the unsaturated ring from becoming aromatic, from C_{13} to C_{12} (compare the bromination of ionene to give trimethylnaphthalene).[47] The conversion of ergopinacol into *neo*ergosterol is similar, but the wandering group is here eliminated altogether, as in the conversion of ionene into dimethylnaphthalene.[48]

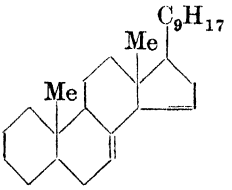
In the above scheme, Rosenheim and King's original formula is used. In the later modification of this there is another methyl group, which could undergo elimination, namely, that attached to C_{10}; this cannot migrate into ring I, since in that event it would be eliminated altogether on oxidation: similarly, it cannot become attached to ring III, because the only carbon atom adjacent to it is that common to rings II and III. A migration from C_{10} to the para-position in ring II would fit the facts, and in that event this ring would become benzenoid. There is some ground for such an assumption, for the evidence of spectrographic work [49] and the behaviour of unimolecular films [50] lend support to a formulation in which the double bonds and the hydroxyl group are closely connected, as in (XL), a formula at one time favoured by I. M. Heilbron.[51] Later, he reverted to the formula (XLI) suggested by A. Windaus, who argues [52] that the double bonds of ergosterol must be conjugated, since ergosterol adds on maleic anhydride, and they cannot, for steric reasons, be situated in two adjacent rings; the addition product has a double bond, which cannot be catalytically hydrogenated, and the conjugated system therefore probably contains the group $CH{:}CR{\cdot}CR'{:}CR''$ or, less probably, $CH{:}CR{\cdot}CH{:}CR'$. The only structures which satisfy these conditions are (XLI) and (XLII) and only the former of these explains the tendency of one of the rings to become aromatic.



(XL.)



(XLI.)



(XLII.)

The structure (XLI) is also supported by the behaviour of ergostadienetriol and methoxyergostadienediol (formed by the action of perbenzoic acid on ergosterol and its methyl ether).[53] These compounds still have the double bond in the side chain, giving methyl*iso*propylacetaldehyde on ozonisation, and also the " inert " double bond characteristic of ergosterol. It follows that their formation involves the addition of hydroxyl in exactly the same positions as that of hydrogen in the first step of the reduction of ergosterol; the " inert " double bond is therefore present in ergosterol and is not formed by the 1 : 4 addition of hydrogen to the conjugated system. Moreover, one of the hydroxyls must be attached to a tertiary carbon, as it resists esterification; [54] the reactive double bond is therefore of the type $>\mathrm{C{:}CH}-$.

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[47] A. von Baeyer and V. Villiger, *Ber.*, 1899, **32**, 2432; *A.*, 1899, i, 921.

[48] L. Ruzicka and E. A. Rudolph, *Helv. Chim. Acta*, 1927, **10**, 916; *A.*, 1928, 63.

[49] T. M. Lowry, *Chem. and Ind.*, 1933, **52**, 10.

[50] N. K. Adam, *ibid.*, p. 12.

[51] *Ibid.*, 1932, **51**, 1061.

[52] *Nach. Ges. Wiss. Göttingen*, **1933**, **94**.

The behaviour of the isomeric α- and β-ergostenols towards perbenzoic acid and catalytically activated hydrogen is strikingly similar to that of *apo*cholic and 3 : 12-dihydroxycholenic acids,[55] and it appears more than likely that the arrangement of the unsaturated centres in these pairs of compounds is identical. Another such pair of compounds is α- and β-ergostene.[56]

Parent Hydrocarbons of the Cholane Group.—As already mentioned (p. 199), the original Rosenheim–King formula was based on the formation of chrysene by the dehydrogenation of cholic (or cholatrienic) acid. Cholesterol and ergosterol under the same conditions gave two hydrocarbons, $C_{18}H_{16}$ and $C_{25}H_{24}$. The C_{18} or " Diels's " hydrocarbon was thought to be hydrochrysene,[57] but this view was later abandoned in favour of a *cyclo*pentenophenanthrene structure;[58] the presence of the phenanthrene nucleus is shown by the great resemblance of the absorption spectrum to that of retene.

Early in the year Ruzicka [59] published the result of a reinvestigation of the whole problem. No chrysene was isolated in any of his experiments, but Diels's hydrocarbon was obtained in every case; moreover, ergosterol yielded a hydrocarbon $C_{26}H_{26}$, the next higher homologue of the hydrocarbon $C_{25}H_{24}$ produced from cholesterol. Diels [60] maintains that chrysene is produced in these dehydrogenations, and it has also been obtained by the distillation of cholesterol and cholic acid with zinc dust;[61] but the point is an academic one, since it is now abundantly clear that chrysene cannot be a *primary* product and its formation therefore gives but little information as to the skeleton of this group. On the other hand, Diels's hydrocarbon has gained additional importance.

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[53] I. M. Heilbron, A. L. Morrison, and J. C. E. Simpson, *J.*, 1933, 302; *A.*, 500.

[54] A. Windaus and A. Lüttringhaus, *Annalen*, 1930, **481**, 119; *A.*, 1930, 1178.

[55] O. Rosenheim and H. King, *Chem. and Ind.*, 1932, **51**, 464; *A.*, 1932, 736; I. M. Heilbron, A. L. Morrison, and J. C. E. Simpson, *loc. cit.*

[56] A. L. Morrison and J. C. E. Simpson, *J.*, 1932, 1710; *A.*, 1932, 845.

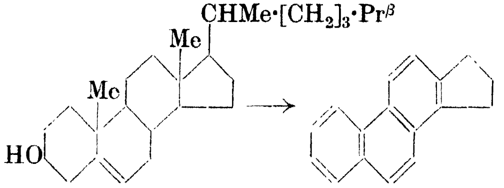
[57] O. Rosenheim and H. King, *Chem. and Ind.*, 1932, **51**, 954; *A.*, 1933, 62.

[58] *Idem, ibid.*, 1933, **52**, 10, 299; *A.*, 497.

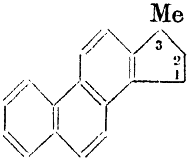
[59] L. Ruzicka and G. Thomann, *Helv. Chim. Acta*, 1933, **16**, 216; L. Ruzicka, M. W. Goldberg, and G. Thomann, *ibid.*, p. 812; *A.*, 278, 820.

[60] *Ber.*, 1933, **66**, [*B*], 487, 1122; *A.*, 606, 1047.

It might have been expected that the dehydrogenation of, say, cholesterol would lead to a compound $C_{17}H_{14}$ (XLIII), rather than $C_{18}H_{16}$:



(XLIII.)



(XLIV.)

The compound (XLIII) has been independently synthesised by three groups of workers,[62, 63, 64] but although J. W. Cook and C. L. Hewett were at first led to believe that it was identical with Diels's hydrocarbon,[65] crystallographic evidence, particularly measurements of the crystal spacing by the *X*-ray method,[66] finally established that they were different. The 1- and the 2-methyl compound were also found to differ from Diels's compound; it is a curious fact that the method of mixed melting points is applicable to these two derivatives but fails with *cyclo*pentenophenanthrene (XLIII).

The synthesis of the 3-methyl compound (XLIV) was announced by E. Bergmann and H. Hillemann,[67] but they did not obtain enough material to settle the question of its identity with Diels's hydrocarbon: this was achieved[68] when a large quantity was synthesised by another method, and comparison of the two compounds, their derivatives, absorption spectra, and crystal spacings left no doubt as to their identity.

The mode of formation of this compound from cholesterol, involving the elimination of a side chain from a saturated *cyclo*pentane ring, followed by migration of a methyl group to the position vacated by the latter, is unusual. The logical explanation would be that the methyl group and the side chain are *both* attached to C_{17}; but such an explanation is at variance with Wieland, Schlichting, and Jacobi's degradation of the cholanic acid side chain [69] and with the facts discussed on p. 206. Further experimental work is clearly desirable on this point, as it has an important bearing on the value of the selenium dehydrogenation method of ascertaining the constitution of natural products.

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[61] H. Raudnitz, F. Petrů, and F. Haurowitz, *Z. physiol. Chem.*, 1932, **209**, 103; *A.*, 1932, 944; H. Raudnitz, F. Petrů, and A. Stadler, *Ber.*, 1933, **66**, [*B*], 878; *A.*, 712.

[62] L. Ruzicka, L. Ehmann, M. W. Goldberg, and H. Hösli, *Helv. Chim. Acta*, 1933, **16**, 833; *A.*, 820.

[63] G. A. R. Kon, *J.*, 1933, 1084; *A.*, 1153.

[64] J. W. Cook and C. L. Hewett, *ibid.*, p. 1099; *A.*, 1043.

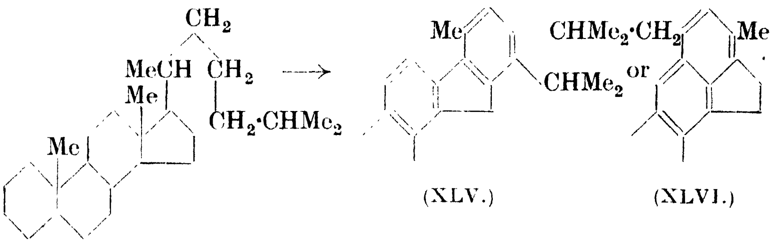
[65] *Chem. and Ind.*, 1933, **52**, 451; *A.*, 710; and *loc. cit.*

[66] J. D. Bernal and D. Crowfoot, *Chem. and Ind.*, 1933, **52**, 729.

[67] *Ber.*, 1933, **66**, 1302; *A.*, 1154.

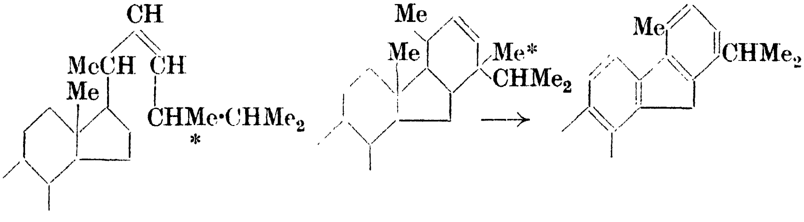
[68] G. A. R. Kon, *Chem. and Ind.*, 1933, **52**, 950; S. H. Harper, G. A. R. Kon, and F. C. J. Ruzicka, *J.*, 1934, 124.

The structure of the second hydrocarbon isolated by Diels is uncertain at present; it is doubtless formed by the cyclisation of the side chain to form the skeleton (XLV) [70] or (XLVI) : [71]



(XLV.) (XLVI.)

The cyclisation of the side chain of ergosterol by the scheme proposed by Rosenheim and King must inevitably lead to the loss of the methyl group marked * when the fifth ring becomes aromatic, and will therefore give the same hydrocarbon as cholesterol; the alternative scheme permits of the higher homologue being formed :



Ruzicka, Goldberg, and Thomann also formulate a hydrocarbon $C_{21}H_{16}$, obtained by them in the dehydrogenation of cholic acid, in the same way as (XLVI) but without the side chain. This compound should be identical with the dehydrogenation product of dehydronorcholene (p. 207): the two compounds, on the contrary, are widely different. The discrepancy will no doubt soon be settled by synthesis.

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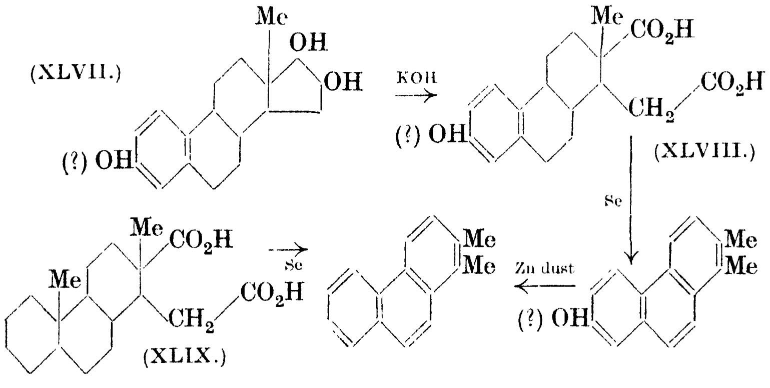
[69] *Z. physiol. Chem.*, 1926, **161**, 80; *A.*, 1927, 247; *Ann. Reports*, 1927, **24**, 130.

[70] O. Rosenheim and H. King, *Chem. and Ind.*, 1933, **52**, 299; *A.*, 497.

[71] L. Ruzicka, M. W. Goldberg, and G. Thomann, *Helv. Chim. Acta*, 1933, **16**, 812; *A.*, 820.

Finally, mention must be made of the extremely interesting substances, œstrone and œstriol,[72] which represent the œstrus-producing hormones of the female. They are discussed in detail in the Biochemistry section of the Reports for 1932 (p. 239); it remains to add that the connexion, merely suspected up to the present, between these substances and those of the cholane group has been definitely established.[73] An acid $C_{18}H_{22}O_5$ (XLVIII), produced by the fusion of œstriol (XLVII) with alkali,[74] passes on dehydrogenation with selenium into a hitherto unknown 1 : 2-dimethylphenanthrol, and this is reduced to 1 : 2-dimethylphenanthrene, the structure of which has been confirmed by synthesis. The same dimethylphenanthrene has also been obtained by the dehydrogenation of ætiobilianic acid (XLIX); this affords the first chemical proof of the phenanthrene-like arrangement of rings I, II, and III in the cholane group.


(XLVII.) (XLVIII.) (XLIX.)

Moreover, it has been shown by Butenandt [75] that pregnanediol, which is a physiologically inactive compound found in the urine during pregnancy, has the structure (L); he suggests that it may be an intermediate formed in the oxidation of a bile acid to the active compounds themselves: [76]

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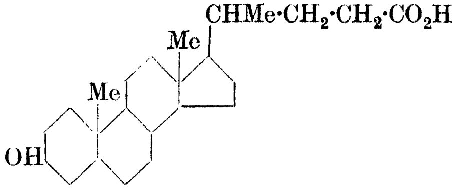
[72] For nomenclature, see *Nature*, 1933, **132**, 205; *A.*, 1048.

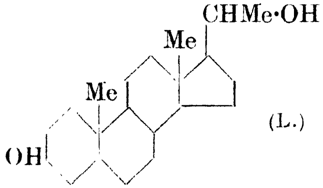
[73] A. Butenandt, H. A. Weidlich, and H. Thompson, *Chem. and Ind.*, 1933, **52**, 268; *Ber.*, 1933, **66**, [*B*], 601; *A.*, 540.

[74] G. F. Marrian and G. A. D. Haslewood, *ibid.*, 1932, **51**, 277T; *A.*, 1932, 1253; E. A. Doisy, *J. Biol. Chem.*, 1933, **99**, 327; *A.*, 278.

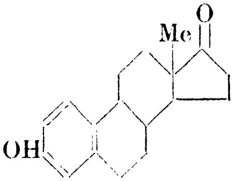
[75] *Ber.*, 1931, **64**, 2529; *A.*, 1932, 54.

[76] *Angew. Chem.*, 1932, **45**, 655.





(L.)



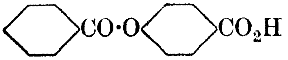
The last stage of the process, in which ring I becomes aromatic, is assumed to involve the loss of a methyl group, as in the formation of *neo*ergosterol (p. 212).

G. A. R. K.

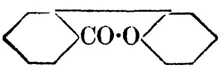
Optical Activity of Diphenyl Derivatives.—This is reported on p. 255.

Lichen Acids and Depsides.

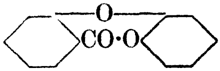
Extraction of lichens, in various ways, yields small quantities of crystalline substances, usually acidic in character and derived from *p*-benzoyloxybenzoic acid (A) : *o*- or *m*-coupling is exceptional.



(A.)



(B.)



(C.)

Variations of this simple depside structure are found where the ester bond is supplemented as in derivatives of diphenylmethylolid (B) and in derivatives of the salazic acid type which appear to contain the diphenyl ether structure (C). Some lichen acids (*e.g.*, usnic acid) appear to contain no depside structure, and (less well authenticated) lichesteric acid and its congeners seem to be lactones of the higher aliphatic hydroxy-acids.

A considerable amount of work was done on lichen acids during the past century,[77] but only when E. Fischer [78] developed suitable methods for synthetic work was the subject put on a sound experimental basis. In the past few years much progress has been made by A. Robertson and his co-workers, who have established the constitutions of a number of depsides by irreproachable synthetic methods. Their work on derivatives of usnic acid is most impressive and seems likely soon to culminate in the synthesis of usnic acid itself. The researches of the Japanese school, chiefly by Y. Asahina and his assistants, are voluminous but largely analytical and lack confirmation by synthesis. No doubt this will be remedied in due course.

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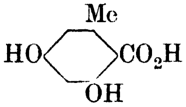
[77] See Perkin and Everest, "Natural Organic Colouring Matters."

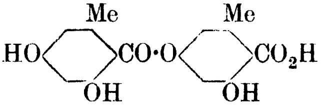
[78] E. Fischer, collected papers, "Untersuchungen über Depside und Gerbstoffe."

In this, the first, report on the subject evernic and barbatic acids and atranorin are discussed in some detail. A shorter account of the more recently examined depsides of simple structure follows; and lichen substances that are either not depsides or depsides of unusual structure are considered last.

Evernic Acid.—Lecanoric acid (II) is derived from two molecules of orsellinic acid (I) and its constitution has been proved by E. Fischer and H. Fischer [79] by synthesis from orsellinic acid. By hydrolysis and simultaneous decarboxylation evernic acid gives orcinol and everninic acid (6-hydroxy-4-methoxy-2-methylbenzoic acid). Fischer [80] showed that, by methylation with diazomethane, evernic acid gives methyl *O*-trimethyl-lecanorate (III): it follows that evernic acid has the constitution (IV). This has now been confirmed by the synthesis of methyl evernate (VII) by A. Robertson and R. J. Stevenson [81] from acetyleverninoyl chloride (V) and methyl orsellinate (VI).

(I.)





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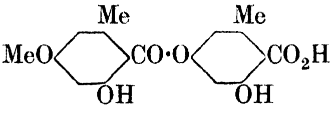

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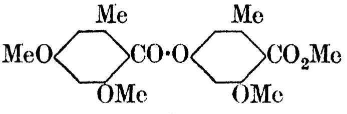
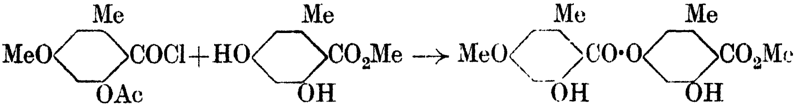


(III.)



(V.) (VI.) (VII.)

Barbatic Acid.—From a study of its decomposition products and by analogy with evernic acid A. St. Pfau [82] concluded that barbatic acid has the constitution (VIII). The correctness of this has recently been shown by A. Robertson and R. J. Stevenson,[83] who have prepared methyl *O*-monomethylbarbatate (XIA), identical in every way with a specimen derived from natural barbatic acid, from *O*-acetylrhizonoyl chloride (IX) and methyl *iso*rhizonate (X). Methyl barbatate, prepared similarly, was also identical with a specimen prepared from the natural product.

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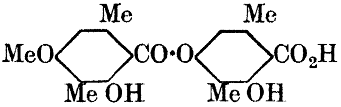
[79] *Ber.*, 1913, **46**, 1138; *A.*, 1913, i, 732.

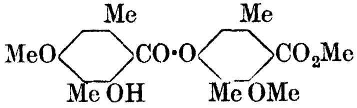
[80] *Ber.*, 1914, **47**, 505; *A.*, 1914, i, 417.

[81] *J.*, 1932, 1388; *A.*, 1932, 742.

[82] *Helv. Chim. Acta*, 1928, **11**, 864; *A.*, 1928, 1241.

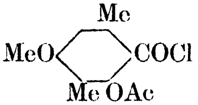


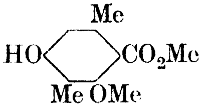
(VIII.)



(XIA.)

(IX.)





(X.)

Atranorin.—This interesting substance has attracted considerable attention. It has been shown by earlier workers [84] to be the methyl ester of a depside. By decomposition with hot alcohols it gives methyl β-orcincarboxylate (β-orcin = xylorcin) and esters of hæmatommic acid; further decomposition of atranorin gives atranol, which is also produced by decomposition of hæmatommic acid. C. Schöpf, K. Heuck, and R. Duntze [85] showed that atranorin is hydrolysed by 23% potassium hydroxide solution to atranol, 2 : 6-dihydroxy-*p*-xylene, and hæmatommic acid. Further, A. St. Pfau [86] obtained atranol from hæmatommic acid by decarboxylation. It is evident that atranol is, so to speak, the kernel of the atranorin structure.

Atranol was shown synthetically by A. Robertson and R. Robinson [87] to be γ-orcylaldehyde (3 : 5-dihydroxy-*p*-tolualdehyde) (XI). Further experiments by F. H. Curd, A. Robertson, and R. J. Stevenson [88] have now established the constitution of atranorin itself. Methyl orsellinate (see I) by treatment with hydrogen cyanide gave the two possible isomeric aldehydes; one of these is identical with methyl hæmatommate (the other is methyl *iso*-hæmatommate); since atranol (XI) results by decarboxylation of hæmatommic acid, this must be the *p*-derivative and therefore the constitution of hæmatommic acid is (XII). Almost simultaneously A. St. Pfau [86] converted ethyl orsellinate by the same method into a mixture of ethyl hæmatommate (identical in every way with the natural product) and ethyl *iso*hæmatommate. Methylation of natural atranorin, followed by hydrolysis, gave methyl *iso*rhizonate (X): unfortunately no atranol residue could be detected, but, since the other part of the molecule is known to be hæmatommic acid, it is to be concluded that atranorin has the structure (XIII).

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[83] *J.*, 1932, 1675; *A.*, 1932, 850.

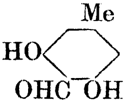
[84] See A. St. Pfau, *Helv. Chim. Acta*, 1926, **9**, 650; *A.*, 1926, 836.

[85] *Annalen*, 1931, **491**, 220; *A.*, 1932, 60.

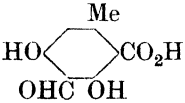
[86] *Helv. Chim. Acta*, 1933, **16**, 282; *A.*, 503.

[87] *J.*, 1927, 2196; *A.*, 1927, 1084.

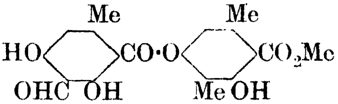
[88] *J.*, 1933, 130; *A.*, 396.



(XI.)



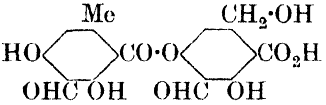
(XII.)



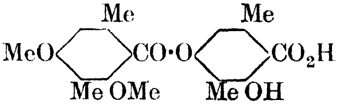
(XIII.)

An interesting corollary to this is provided by Y. Asahina and T. Tukamoto,[89] who report the conversion of atranorin into methyl norbarbatate (see VIII) by catalytic hydrogenation (reduction of CHO to Me).

Barbatolic Acid.—By hydrolysis and simultaneous decarboxylation barbatolic acid gives atranol (XI) and 3 : 5-dihydroxy-4-formylbenzyl alcohol. From these results and by analogy with atranorin the probable structure of the depside is given by C. Schöpf, K. Heuck, and R. Duntze [85] as (XIV).



(XIV.)



(XV.)

Diffractaic or Dirhizonic Acid.—Since diffractaic acid yields carbon dioxide, β-orcinol and rhizonic acid methyl ether (see X) on hydrolysis, Y. Asahina and F. Fuzikawa [90] concluded that it is a methyl ether (XV) of barbatic acid (VIII). They confirmed their view by the synthesis of methyl diffractate,[91] identical with a specimen prepared from the natural acid, from dimethyl-β-orcinolcarboxyl chloride methyl ether [rhizonoyl chloride methyl ether (see IX)] and methyl β-orcinolcarboxylate. Finally [92] they identified diffractaic acid with the dirhizonic acid of O. Hesse.[93] [The name dirhizonic acid is a misnomer, for the depside is derived from one molecule of rhizonic acid methyl ether and one of 3 : 5-dihydroxy-*p*-xylenecarboxylic acid. Dirhizonic acid would be an *o*-didepside derived from two molecules of rhizonic acid (see IX).]

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[89] *Ber.*, 1933, **66**, [*B*], 897; *A.*, 823.

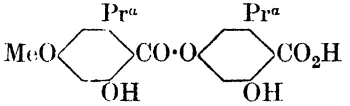
[90] *Ber.*, 1932, **65**, [*B*], 175; *A.*, 1932, 396.

[91] *Ibid.*, p. 583; *A.*, 1932, 613.

[92] *Ibid.*, p. 1668; *A.*, 69.

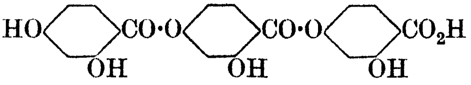
[93] *J. pr. Chem.*, 1906, [ii], **73**, 120; *A.*, 1906, i, 280.

Divaricatic Acid.—The constitution (XVI) for divaricatic acid has been established in the following way. Hydrolysis of the natural product with cold dilute alkali solution produces, according to Hesse,[94] divaricatinic acid and divaric acid. The phenol (divarin) corresponding to divaric acid (compare atranol and hæmatommic acid) has been shown synthetically by A. Sonn and B. Scheffler [95] and by F. Mauthner [96] to be 3 : 5-dihydroxy-*n*-propylbenzene. Divaricatinic acid has been identified by Sonn [97] as a methyl ether of divaric acid. Hence, by analogy with other depsides (compare evernic and barbatic acids) the constitution shown has been adopted. The results obtained by Y. Asahina and T. Hirakata [98] are in harmony with the above. Methylation of divaricatic acid with diazomethane gave methyl divaricatate dimethyl ether, and this, by fission with methyl-alcoholic potash, produced 2 : 4-dimethoxy-6-propylbenzoic acid and methyl 4-hydroxy-2-methoxy-6-propylbenzoate.



(XVI.)

Gyrophoric Acid.—This depside is of particular interest in that it is one of the few natural tridepsides. On hydrolysis gyrophoric acid gives orsellinic acid only, and Hesse [99] therefore considered that it was isomeric with lecanoric acid (II). However, the synthesis, by E. Fischer and H. Fischer,[1] of the possible isomeric diorsellinic acids rendered this view untenable, for, although the *p*-isomeride was identical with lecanoric acid, *o*-diorsellinic acid was not identical with gyrophoric acid. Moreover, values for the molecular weight were consistently high and Hesse [2] therefore considered doubling the accepted value for the formula. Y. Asahina and M. Watanabe,[3] from a careful analytical examination of the depside, came to the conclusion that it was *pp*-triorsellinic acid (XVII) and, later, Y.

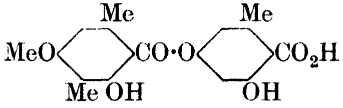


(XVII.)

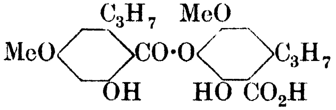
[94] *J. pr. Chem.*, 1911, [ii], **83**, 25; *A.*, 1911, i, 208.
[95] *Ber.*, 1924, **57**, [*B*], 959; *A.*, 1924, i, 849.
[96] *J. pr. Chem.*, 1924, [ii], **107**, 103; *A.*, 1924, i, 524.
[97] *Ber.*, 1931, **64**, [*B*], 1851; *A.*, 1931, 1055.
[98] *Ber.*, 1932, **65**, [*B*], 1665; *A.*, 64.
[99] *J. pr. Chem.*, 1900, [ii], **63**, 463; *A.*, 1901, i, 85.
[1] *Ber.*, 1913, **46**, 1142; *A.*, 1913, i, 732.
[2] *J. pr. Chem.*, 1915, [ii], **92**, 466; *A.*, 1916, i, 264.
[3] *Ber.*, 1930, **63**, [*B*], 3044; *A.*, 1931, 221.

Asahina and F. Fuzikawa [4] confirmed this view by the synthesis of methyl gyrophorate tetramethyl ether from orsellinoyl chloride dimethyl ether and methyl lecanorate and methylation of the product. F. W. Canter, A. Robertson, and R. B. Waters [5] obtained methyl gyrophorate tetramethyl ether directly, by the condensation of orsellinoyl chloride dimethyl ether and methyl *O*-dimethyllecanorate of known constitution. The constitution of gyrophoric acid is, then, very fully confirmed.

Obtusatic or Ramalic Acid.—Previously reported on by several workers, obtusatic acid has now given fission products which indicate that it has the constitution (XVIII). By methylation Y. Asahina and F. Fuzikawa [6] obtained a trimethyl derivative, which, by hydrolysis, gave rhizonic acid methyl ether (see IX) and *iso*everninic acid (4-hydroxy-6-methoxy-2-methylbenzoic acid). Ramalic acid has been hydrolysed by G. Koller [7] to orsellinic and rhizonic acids; therefore it is, at least, isomeric with obtusatic acid. Its identity with obtusatic acid was finally shown by G. Koller and G. Pfeiffer,[8] who, by hydrolysis with methyl alcohol, obtained as a fission product, methyl rhizonate and not methyl orsellinate.



(XVIII.)



(XIX.)

Sekakaic Acid.—Based on their analytical results, Y. Asahina and S. Nonomura [9] suggest the *m*-didepside structure (XIX) for this acid. By methylation with diazomethane and hydrolysis of the resulting methyl sekakaate dimethyl ether, there are obtained divaricatinic acid methyl ether and methyl hydroxydivaricatinate methyl ether. The latter, by decarboxylation, yields an oily phenol, which is acetylated to 3 : 5-dimethoxy-4-acetoxypropylbenzene. The constitution of divaricatic acid being known (see p. 221), the suggested formula is in agreement with the analytical results obtained. The Reporter considers that much further confirmation is required, preferably by synthetic work, and, at least partly, on the grounds of the unusual, but not exceptional, *m*-didepside structure (the *m*-didepside structure is known to be present in the gallotannin molecule).[10]

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[4] *Ber.*, 1932, **65**, [*B*], 983; *A.*, 1932, 851.

[5] *J.*, 1933, 493; *A.*, 713.

[6] *Ber.*, 1932, **65**, [*B*], 580; *A.*, 1932, 613.

[7] *Monatsh.*, 1932, **61**, 286; *A.*, 1932, 1252.

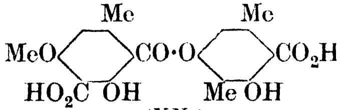
[8] *Ibid.*, 1933, **62**, 241; *A.*, 715.

[9] *Ber.*, 1933, **66**, [*B*], 30; *A.*, 159.

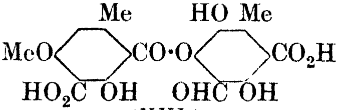
[10] See Fischer, "Untersuchungen über Depside und Gerbstoffe."

*Squamatic and iso**Squamatic Acids.*—The empirical formula $C_{19}H_{20}O_9$ for squamatic acid, formerly adopted, has been corrected to $C_{19}H_{18}O_9$ by Y. Asahina and M. Yanagita,[11] who have proved the presence of two carboxyl groups by titration. By hydrolysis and simultaneous decarboxylation there result the monomethyl ether of orcinoldicarboxylic acid and β-orcinol (xylorcin). Methylation with diazomethane and hydrolysis of the product gives the dimethyl ether of orcinoldicarboxylic acid and methyl *iso*rhizonate (X). These results indicate the structure (XX) for the depside. The very close resemblance of this formula to that of atranorin suggests that the depside may be a methyl ether of atranorin, partial oxidation accounting for the higher oxygen content of squamatic acid, the more so since the presence of two free carboxyl groups is proved only by titration and depsides are very feebly acidic, being scarcely soluble in bicarbonate solution. Further confirmation is urgently needed.

Y. Asahina and M. Yanagita [12] describe a new depside, *iso*squamatic acid, differing from squamatic acid only in the exchange of the hydroxyl and the methoxyl group in the orcinoldicarboxylic acid nucleus.



(XX.)



(XXI.)

Thamnolic Acid.—By hydrolysis and simultaneous decarboxylation thamnolic acid gives orcinoldicarboxylic acid monomethyl ether and thamnol. Thamnol is 2 : 5 : 6-trihydroxy-4-methylbenzaldehyde and not the isomeric 3 : 5 : 6-trihydroxy-4-methylbenzaldehyde; this is likely by analogy with atranol (XI) and was established by Y. Asahina and F. Fuzikawa [13] through the conversion of atranol into thamnol in the following way : Atranol was coupled with benzenediazonium chloride, and the resulting azo-compound reduced to the amine, treatment of which with concentrated alkali solution gave the corresponding phenol, identical with thamnol. The previous suggestion by Y. Asahina and S. Ihara [14] that the depside has the structure (XXI) is in harmony with this. Further work by Y. Asahina and S. Ihara [15] confirms the views previously put forward. Exhaustive methylation of thamnolic acid, followed by hydrolysis of the amorphous pentamethyl compound gives 3 : 5-dimethoxytoluene-2 : 4-dicarboxylic acid, indicating that one of the carboxyl groups of the orcinol nucleus is esterified with one of the hydroxyl groups of the thamnol nucleus and not vice versa. Analogy with other depsides suggests that the structure is probably correct, but again more work is necessary.

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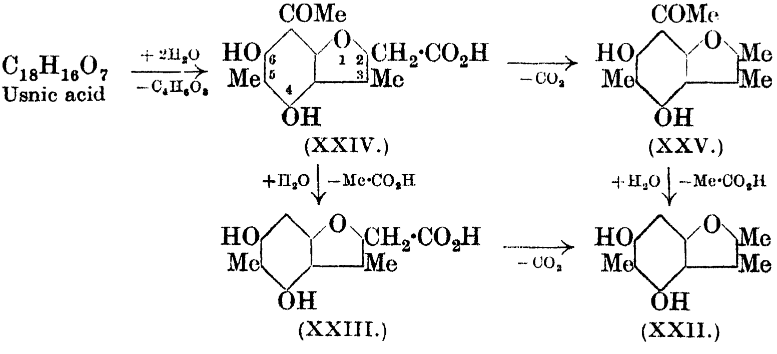
[11] *Ber.*, 1933, **66**, [*B*], 36; *A.*, 159.
[12] *Ibid.*, p. 393; *A.*, 504.
[13] *Ber.*, 1932, **65**, [*B*], 58; *A.*, 1932, 275.
[14] *Ber.*, 1929, **62**, [*B*], 1196; *A.*, 1929, 818.
[15] *Ber.*, 1932, **65**, [*B*], 55; *A.*, 1932, 275.

Usnic Acid.—This acid, $C_{18}H_{16}O_7$, has been isolated from numerous lichen substances. By hydrolysis with alkali are produced acetoacetic acid and usnetic acid, $C_{14}H_{14}O_6$, which is decarboxylated to usnetol, $C_{13}H_{14}O_4$. This phenol loses an acetyl group on treatment with concentrated alkali solution, producing usneol, $C_{11}H_{12}O_3$.

The constitution of usneol has been established by F. H. Curd and A. Robertson,[16] by the synthesis of its ethers, as 4 : 6-dihydroxy-2 : 3 : 5-trimethylcoumarone (XXII). On various grounds it was considered by Curd and Robertson [17] that usnetol was the corresponding 7-acetyl derivative (XXV) and not a substance with a hemiquinonoid structure, as suggested by C. Schöpf and K. Heuck,[18] and this was shown to be correct by the synthesis of *O*-methylusnetol, identical in all respects with the natural product. Usnetic acid (XXIV) is an usnetolcarboxylic acid and its constitution is limited to two possibilities from its conversion into pyrousnic acid by deacetylation. Pyrousnic acid does not form a lactone, is decarboxylated to usneol, and is therefore usneol-2 (or 3)-carboxylic acid and not usneol-5-carboxylic acid. Usnetic acid must be 7-acetylpyrousnic acid.

The relation established between these interesting compounds by Curd and Robertson may thus be summarised :



Alectoronic Acid,[19] *Collatolic Acid,*[20] *and Olivetoric Acid.*[21, 22]—These acids have been examined analytically, through their fission products, and, with the possible exception of olivetoric acid, do not appear to contain the depside group. The Reporter feels that discussion of the suggested structures should be deferred until further work has been done. This is all the more necessary since they, in general, resemble usnic acid, of which the essential structure has been established, and occur in the same lichens. The suggested structures do not resemble the usnic acid skeleton.

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[16] *J.*, 1933, 714; *A.*, 832. [17] *Ibid.*, p. 1174; *A.*, 1167.

[18] *Annalen*, 1927, **459**, 233; *A.*, 1928, 294.

[19] Y. Asahina and A. Hashimoto, *Ber.*, 1933, **66**, [*B*], 641; *A.*, 714.

[20] Y. Asahina, Y. Kanaoka, and F. Fuzikawa, *ibid.*, p. 649; *A.*, 714.

[21] Y. Asahina and J. Asano, *Ber.*, 1932, **65**, [*B*], 475; *A.*, 1932, 521.

[22] *Idem*, *ibid.*, p. 584; *A.*, 1932, 620.

Salazic Acid Group.—The various acids included in this group are salazic acid,[23, 24, 25, 26] cetraric acid,[25, 27] stictic acid,[28, 29] psoromic acid,[30] and capraric acid.[31] Their relationship is based on the interconversion of various derivatives and the structures at first suggested,[23, 27] improbable if only on the grounds of their containing a nine-membered ring of seven carbon atoms and two oxygen atoms, have recently been replaced [28] by structures containing the depside group (C). Their detailed constitutions are founded solely on the examination of fission products. In view of these facts, discussion is withheld for further confirmation.

Lichesteric,[32] *Protolichesteric,*[32] *Caperatic,*[33] *and Alignic* [34] *Acids.*—These acids, isolated from various lichens, appear to be non-aromatic in character. On various analytical grounds they are formulated as lactones (or the free acids) of the higher aliphatic hydroxy-acids. The work has not been sufficiently advanced to justify the preparation of a report.

T. Currie and A. Russell [35] have prepared a number of simple depside methyl ethers by condensation of an acid chloride with the sodium salts of hydroxy-aldehydes and oxidation of the resulting aldehydes. Since these are connected with another problem,[36] discussion under the present heading is not relevant. R. O. Pepe [37] describes the preparation of various phenol esters of substituted gallic acids by the action of the phenol on the acid azide. A. R.

G. A. R. Kon.
Alfred Russell.

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[23] Y. Asahina and J. Asano, *Ber.*, 1933, **66**, [*B*], 689; *A.*, 714.

[24] *Idem, ibid.*, p. 893; *A.*, 823.

[25] *Idem, ibid.*, p. 1031; *A.*, 824.

[26] *Idem, ibid.*, p. 1215; *A.*, 1161.

[27] Y. Asahina and Y. Tanase, *ibid.*, p. 700; *A.*, 714.

[28] Y. Asahina, M. Yanagita, and T. Omaki, *ibid.*, p. 943; *A.*, 824.

[29] Y. Asahina, M. Yanagita, T. Hirakata, and M. Ida, *ibid.*, p. 1080; *A.*, 1050.

[30] Y. Asahina and H. Hayashi, *ibid.*, p. 1023; *A.*, 824.

[31] Y. Asahina and M. Yanagita, *ibid.*, p. 1217; *A.*, 1161.

[32] M. Asano and T. Kanematsu, *Ber.*, 1932, **65**, [*B*], 1175; *A.*, 1932, 931.

[33] M. Asano and Z. Ohta, *Ber.*, 1933, **66**, [*B*], 1020; *A.*, 823.

[34] T. Dillon and A. McGuinness, *Sci. Proc. Roy. Dublin Soc.*, 1932, **20**, 129; *A.*, 1932, 931.

[35] *J.*, 1932, 2263; *A.*, 1932, 1030.

[36] *J.*, 1933, 140; *A.*, 393.

[37] *J. pr. Chem.*, 1930, [ii], **126**, 241; *A.*, 1930, 1030.

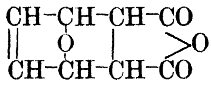
PART III.—HETEROCYCLIC DIVISION.

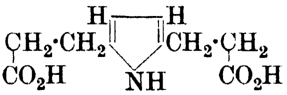
Diene Syntheses in Heterocyclic Nitrogenous Compounds.

THE discovery by O. Diels and K. Alder in 1928 that a conjugated series of double bonds, a " diene " system, could combine additively in the 1 : 4-positions with other substances containing the group $\cdot CH{:}CH\cdot CO$, such as maleic anhydride, citraconic anhydride, acraldehyde, acrylic ester, and *p*-benzoquinone, has been noticed in a previous *Report.*[1] This additive property has proved of great value as a new method of synthesis and also as a diagnostic agent for a conjugated series of double bonds. During the last three years the same authors, following the main theme, have opened up unexpected developments among heterocyclic compounds to which fairly detailed consideration is necessary on account of their great potentialities.

Although furan, as a diene system, adds on maleic anhydride in the same way as has been amply exemplified in other cyclic and non-cyclic diene systems, giving the substance (I), the nitrogenous analogue, pyrrole, behaves differently.[2] Maleic acid and pyrrole in aqueous solution react at room temperature, and from the product a small quantity of pyrroledipropionic acid (II) and dilævulic acid (III) in quantity can be isolated. The mechanism of the reaction is elucidated by a study of 2-methylpyrrole, which yields 2-methylpyrrole-5-succinic acid (IV). This acid, in warm solution, readily loses carbon dioxide to form 2-methylpyrrole-5-propionic acid (V), the constitution of which is established by independent synthesis. The formation of pyrrole-2 : 5-dipropionic acid (II) from pyrrole must accordingly be attributed to decarboxylation of an intermediate tetracarboxylic acid analogous to (IV), and

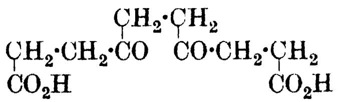
(I.)



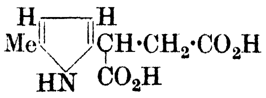


(II.)

(III.)

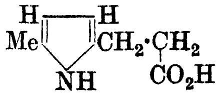


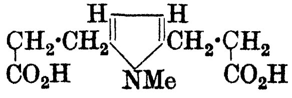
$$\begin{array}{l} \qquad\qquad\quad CH_2\cdot CH_2 \\ CH_2\cdot CH_2\cdot CO \quad CO\cdot CH_2\cdot CH_2 \\ CO_2H \qquad\qquad\qquad\qquad CO_2H \end{array}$$



(IV.)

(V.)





(VI.)

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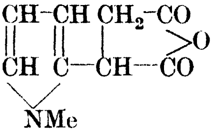
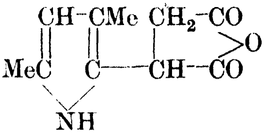
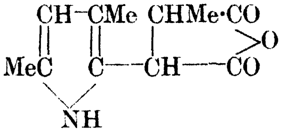
[1] *Ann. Reports,* 1930, **27,** 88.

[2] O. Diels and K. Alder, *Annalen,* 1931, **486,** 211; *A.,* 1931, 849.

dilævulic acid (III) must arise by hydrolysis of (II). In the case of 1-methylpyrrole, the 1-methylpyrrole-2 : 5-dipropionic acid (VI) formed is much more resistant to hydrolysis, so the proportion of dilævulic acid found is very small. The products from 1-methylpyrrole and 2 : 4-dimethylpyrrole with maleic anhydride and citraconic anhydride in non-aqueous solvents have the following constitutions :

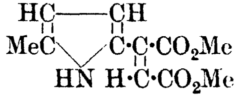


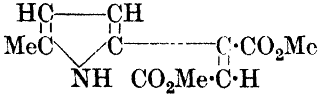




In all these cases addition takes place at one end of the conjugated system with a transference of hydrogen. To the same category belongs the addition of acetylenedicarboxylic acid and its esters to pyrroles.[3] 2-Methylpyrrole and methyl acetylenedicarboxylate combine additively at room temperature to yield two stereoisomeric dimethyl esters (VII) and (VIII), which stand in a *cis-trans* relationship to one another since on catalytic reduction they both yield the same 2-methylpyrrole-5-succinic acid (IV). 2 : 3-Dimethyl- and 2 : 3 : 4-trimethyl-pyrrole behave similarly. 1-Methylpyrrole and acetylenedicarboxylic acid also combine in molecular proportion to give 1-methylpyrrole-2-maleic acid and its anhydride, but 2 : 4-dimethylpyrrole and 1-methylindole form products, (IX) and (X) respectively, containing two molecules of the nitrogenous component.

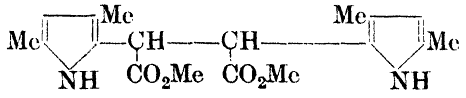
(VII.)

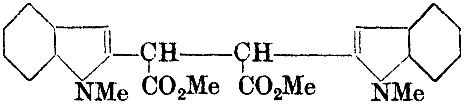




(VIII.)

(IX.)





(X.)

If, however, methyl acetylenedicarboxylate be allowed to react with 1-methylpyrrole, it does so primarily additively with transference of hydrogen and then the product undergoes a typical 1 : 4-addition of acetylenedicarboxylic ester to yield (XI).

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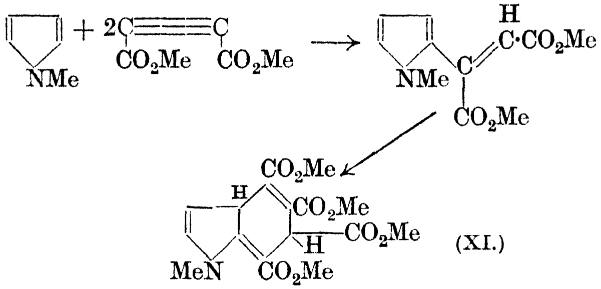
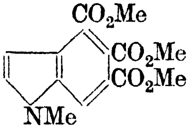
[3] O. Diels and K. Alder, *Annalen*, 1931, **490**, 267; 1932, **498**, 1; *J.*, 1931, 1428; 1932, 1144.

Alternative mechanisms, however, suggest themselves. By the action of bromine on the ester (XI) a structural change takes place

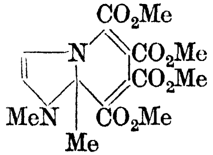


(XI.)

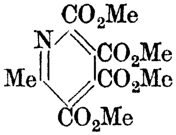
with formation of 1-methylindoletricarboxylic ester (XII), which can be hydrolysed and degraded to 1-methylindole.



(XII.)

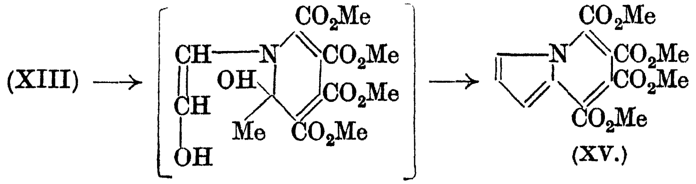


(XIII.)



(XIV.)

4-Methylglyoxaline, pyrazole, and 3 : 5-dimethylpyrazole appear to react additively with transference of hydrogen, but 1 : 2-dimethylglyoxaline initiates a new additive principle. Two molecules of methyl acetylenedicarboxylate combine additively with 1 : 2-dimethylglyoxaline in ethereal solution at room temperature to give an alizarin-red coloured derivative of 1 : 8-dihydropyriminazole (XIII), for, by the action of bromine, the latter is converted into a very stable tetracarboxylic ester of α-picoline (XIV). Another remarkable change undergone by (XIII) is its conversion spontaneously by the action of acetic acid with loss of methylamine into a tetracarboxylic ester of pyrrocoline (XV).

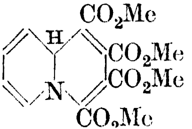


(XV.)

The additive principle underlying the formation of (XIII) is the addition of two molecules of acetylenedicarboxylic ester to the double bond $-\overset{|}{C}{=}N-$, and subsequent developments have shown that the same principle is followed by pyridine, quinoline, *iso*-

quinoline, and stilbazole. The implications of this discovery need no emphasis; to be able to add a straight chain of four carbon atoms to a $-\overset{|}{C}=N-$ bond with production of a new ring is a most valuable weapon in synthetic chemistry. It has been applied by Diels and Alder,[4] incidentally to a determination of the structure of the additive products with pyridine, to the synthesis of coniine, norlupinane, and ψ-lupinine.

Methyl acetylenedicarboxylate and pyridine combine in ethereal solution to yield methyl pyridocoline-1 : 2 : 3 : 4-tetracarboxylate (XV), which is oxidised by hydrogen peroxide to picolinic acid *N*-oxide (XVI); one point of attachment of methyl acetylenedicarboxylate is therefore the α-position. Dilute nitric acid, however, effects a partial degradation of the molecule with liberation of oxalic acid, the other product being methyl pyrrocoline-1 : 2 : 3-tricarboxylate (XVII), since it can be hydrolysed and then decarboxylated to pyrrocoline, also known as pyrindole or indolizine (XVIII). This base on catalytic reduction yields octahydropyrrocoline (piperolidine) (XIX), which by the action of cyanogen bromide, debromination, and subsequent hydrolysis gives *dl*-coniine (XX).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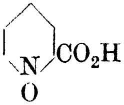
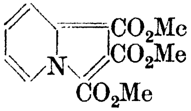
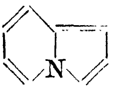
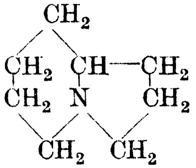

(XVI.)


(XVII.)


(XVIII.)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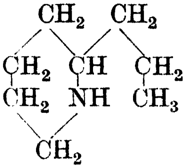
(XX.)

The mechanism of the action of nitric acid on the tetramethyl ester (XV) has been elucidated by a study of the intermediate products. The first substance to be formed is an ester salt (XXI), which is readily hydrolysed to a hydroxy-nitrate (XXII) by water. If this product is treated with perchloric acid, it passes into the perchlorate of a pyridinium ion (XXIII) with simultaneous loss of water. The reactivity or lability of the hydroxy-nitrate (XXII) is the key to the degradation to the indolizine ring system which is convincingly explained by Diels and Alder as a wandering of the

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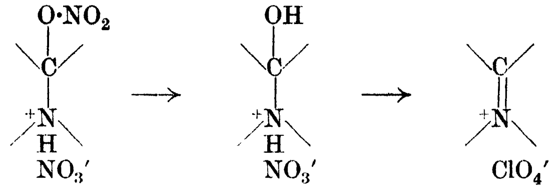
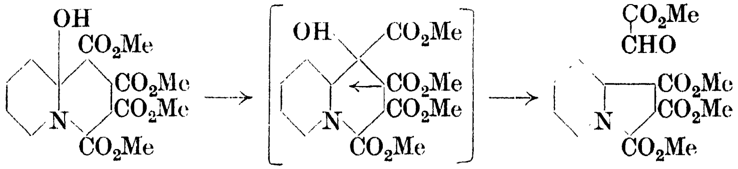
[4] *Annalen*, 1932, **498**, 16; 1933, **505**, 103; *A.*, 1932, 1144; 1933, 1058.

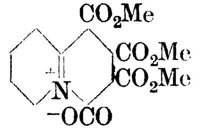


(XXI.) (XXII.) (XXIII.)

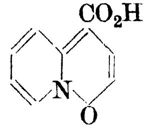
hydroxyl group and a pinacolin-like rearrangement according to the following scheme.



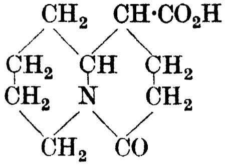
The pyridinium perchlorate (XXIII) is converted into a substance (XXIV), called "Kashimoto's substance" after its discoverer, by the action of pyridine, and the converse can be effected by treatment with sodium methoxide and subsequent acidification with perchloric acid. This internal salt or betaine is converted by



(XXIV.)



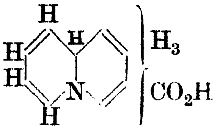
(XXV.)



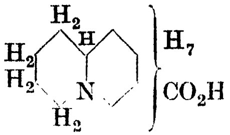
(XXVI.)

warming with sulphuric acid into the lactam (XXV), which can be catalytically reduced to its octahydro-derivative (XXVI). The keto-group is resistant to Clemmensen reduction, but the decarboxylation product of (XXVI) on drastic reduction with sodium and amyl alcohol gives, not the expected octahydropyridocoline, but octahydropyrrocoline (XIX).

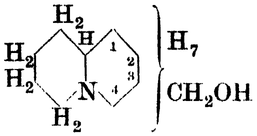
The degradation of methyl pyridocolinetetracarboxylate (XV) to norlupinane is described under the section dealing with lupin alkaloids, but another change which deserves notice is its hydrolysis



(XXVII.)



(XXVIII.)

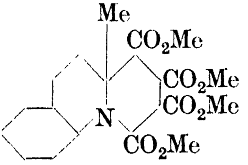


(XXIX.)

by hydrochloric acid with loss of three carboxyl groups to a monocarboxylic acid (XXVII).

On catalytic hydrogenation this takes up eight hydrogen atoms with formation of an acid (XXVIII), from which a methyl ester was prepared. A Bouveault and Blanc reduction of this ester gave an alcohol, *ψ*-lupinine (XXIX), which was characterised by crystalline derivatives, but these proved to be different from those of lupinine or *iso*lupinine (*epi*lupinine) of natural origin. The conclusion is drawn that the carboxyl group cannot therefore be in the 1-position as in lupinine. This deduction is justified if there are only two lupinines, as there should be if the nitrogen atom is planar. In a later section this point is dealt with more fully.

Since quinaldine combines with two molecules of methyl acetylenedicarboxylate in the same way as pyridine to yield the tetramethyl ester (XXX), where movement of a hydrogen atom is precluded,



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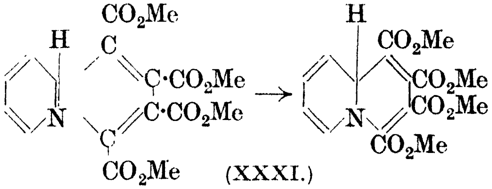


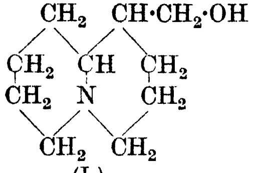
(XXXI.)

Diels and Alder suggest that addition to the $-\overset{|}{C}{=}N-$ link is not a two-stage process beginning with a reaction of the nitrogenous compound but rather addition of a double methyl acetylenedicarboxylate molecule with terminal free valencies to the $-\overset{|}{C}{=}N-$ link as shown diagramatically in (XXXI). In support of this mechanism are the observations that in all cases two molecules of ester are added and that under somewhat changed conditions, if ether is replaced by acetic acid as a solvent for methyl acetylenedicarboxylate, small additions of pyridine catalyse the two-stage polymerisation of methyl acetylenedicarboxylate, which then adds on a third molecule of ester with production of the hexamethyl ester of mellitic acid, $C_6(CO_2Me)_6$.

Alkaloids.

Piperidine Group.—A great clarification has taken place in the group of lupin alkaloids during the past two years. The simplest member of the group is lupinine and the most favoured formula, put forward by Karrer in 1928 on the basis of exhaustive methylation, degradation, and reduction, was (I). This received strong support from the observations of K. Winterfeld and F. W.

Holschneider,[5] who found that lupinane (II) on treatment with cyanogen bromide gave 1-cyano-3-methyl-2-ω-bromobutylpiperidine (III), as was shown by its conversion into pyridine-2 : 3-dicarboxylic acid and other products. If the nitrogen atom in lupinine is non-planar, the possibility of *cis-trans* isomerism about the $\rangle C{-}\overset{|}{N}{-}$ hinge must be admitted and there will be four racemic forms of this substance. The parent base, norlupinane (IV), will occur in two non-resolvable forms each with a plane of symmetry, but in the case of a keto-derivative, *e.g.*, (XIII), there will be two racemates. The possibility, therefore, of substantiating formula (I) by synthetic experiments was not immediately practicable, but the synthesis of the parent substance norlupinane (IV), also known as octahydropyridocoline or octahydroquinolizine, has been effected.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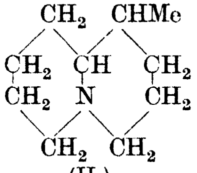
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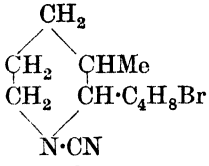
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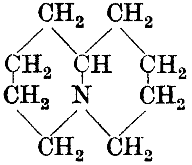
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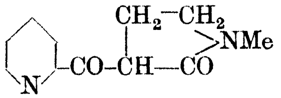
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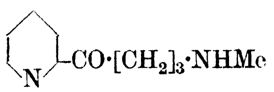
(VI.)

Lupinine can be converted into the well-characterised norlupinane (IV) either by soda-lime distillation of lupininic acid,[6] followed by reduction of the basic fraction with palladium and hydrogen, or by a Curtius breakdown of lupininehydrazide.[7] An identical product has been obtained synthetically by K. Winterfeld and F. Holschneider[8] in the following way. 2-Pyridyl 1-methyl-2-pyrrolidonyl-3 ketone (V), prepared by condensation of α-picolinic ester and 1-methyl-2-pyrrolidone, on ketone hydrolysis gave 2-γ-methylaminobutyrylpyridine (VI), the benzoyl derivative of which was reduced catalytically in presence of platinum oxide to the secondary alcohol of the corresponding piperidine derivative (VII). By the action of phosphorus pentabromide on this substance

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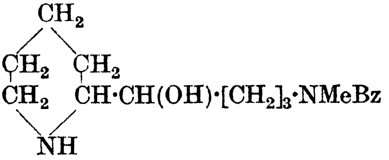
[5] *Ber.*, 1931, **64**, [*B*], 137; *A.*, 1931, 370.

[6] G. R. Clemo and G. R. Ramage, *J.*, 1931, 437; *A.*, 1931, 499.

[7] G. R. Clemo, G. R. Ramage, and R. Raper, *ibid.*, p. 3191; *A.*, 1932, 178; *J.*, 1932, 2963; *A.*, 169.

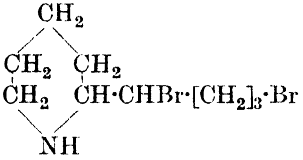
[8] *Annalen*, 1932, **499**, 109; *A.*, 78.

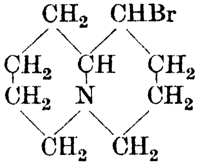
2-αδ-dibromobutylpiperidine (VIII) was obtained with loss of benzonitrile and methyl bromide. This bromide (VIII) was cyclised



(VII.)

(VIII.)

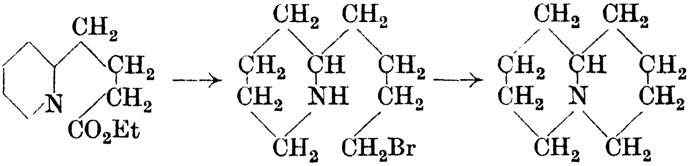




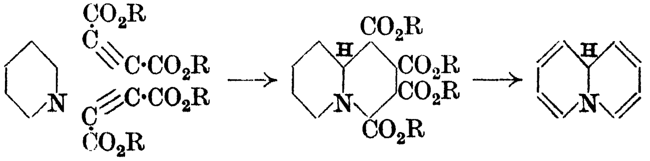
(IX.)

by the action of sodium ethoxide to 1-bromo-octahydropyridocoline (IX), which could be reduced catalytically to octahydropyridocoline, identical in all its properties with norlupinane (IV).

A second, elegant synthesis was effected by G. R. Clemo, G. R. Ramage, and R. Raper [9] by subjecting ethyl γ-2-pyridylbutyrate to a combined Bouveault and nuclear reduction, followed by halogenation, and cyclisation by withdrawal of hydrogen halide, thus:



Yet a third synthesis has been effected by O. Diels and K. Alder [10] from acetylenedicarboxylic ester and pyridine, which combine at room temperature to give quinolizine-1 : 2 : 3 : 4-tetracarboxylic ester (X). This was degraded in stages to a mixture of bases



(X.) (XI.)

which contained quinolizine (XI), and this on complete catalytic reduction gave octahydroquinolizine. The picrate seemed to be identical with that of norlupinane, but there were differences in the aurichlorides.

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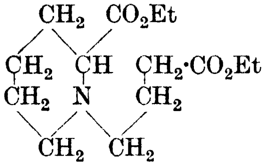
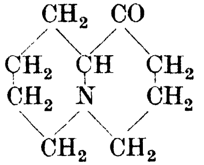
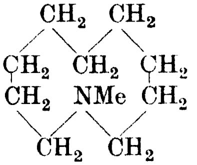
[9] *J.*, 1932, 2960; *A.*, 169.

[10] *Annalen*, 1932, **498**, 21; 1933, **505**, 119; *A.*, 1932, 1144; 1933, 1058.

In addition to the above successful syntheses one other has been effected leading to a different product; the consequences are, however, important. G. R. Clemo and G. R. Ramage [11] obtained an isomeric octahydropyridocoline B from the dicarboxylic ester (XII) by the Dieckmann reaction, followed by hydrolysis to 1-keto-octahydropyridocoline (XIII) and a Clemmensen reduction of the latter. A study of the Hofmann reduction by G. R. Clemo, G. R. Ramage, and R. Raper [12] on norlupinane and octahydropyridocoline B shows that they are stereoisomerides of the *cis-trans* decalin type with non-planar nitrogen, in that they give, among other products,

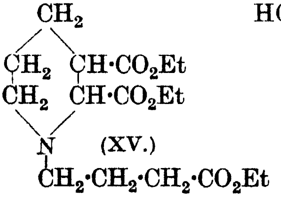

(XII.)

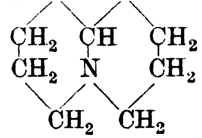

(XIII.)

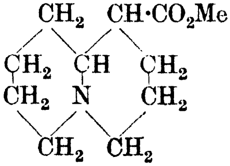

(XIV.)

the same 1-methyl*cyclo*azadecane (XIV). Octahydropyridocoline in occurring in two stereoisomerides thus falls into line with its lower homologue, octahydropyrrocoline, which on synthesis was found to occur in two forms.[13]

These results probably provide an explanation for some observations made by G. R. Clemo, G. R. Ramage, and R. Raper [14] in an attempt to prepare lupininic acid. The ester prepared by condensing ethyl piperidine-2 : 3-dicarboxylate with γ-bromobutyronitrile was converted into the tricarboxylic ester (XV) by the action of alcoholic hydrogen chloride and then submitted to the Dieckmann reaction. The product on hydrolysis and loss of carbon dioxide gave rise to 9-keto-octahydropyridocoline-1-carboxylic acid (XVI),


(XV.)


(XVI.)


(XVII.)

which was reduced by Clemmensen's method and then esterified to methyl octahydropyridocoline-1-carboxylate (XVII). This did not appear to be identical with methyl lupininate or *epi*lupininate of natural origin. It is perhaps significant that the Dieckmann reaction on both occasions has given substances differing from the natural products. If the structure given to (XVII) is correct, then methyl lupininate and methyl *epi*lupininate correspond to two out of the four possible racemates, whilst the synthetic product must be at least one of the two remaining racemates.

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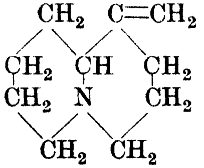
[11] *J.*, 1932, 2969; *A.*, 164.

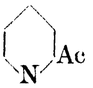
[12] *Ibid.*, p. 2959; *A.*, 169.

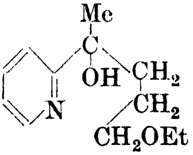
[13] G. R. Clemo and G. R. Ramage, *ibid.*, p. 2969; *A.*, 164.

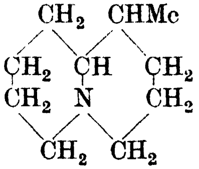
[14] *J.*, 1931, 3192; *A.*, 1932 178.

Final confirmation of the Karrer formula (I) for lupinine has been recently obtained by the synthesis of β-lupinane by K. Winterfeld and F. W. Holschneider.[15] When the elements of water are withdrawn from lupinine, anhydrolupinine (XVIII) is formed and this base on reduction gives a mixture of two stereoisomerides, α- and β-lupinane. The synthesis of the latter was effected by a Grignard reaction between methyl 2-pyridyl ketone (XIX) and γ-bromopropyl ethyl ether with formation of methyl-ω-ethoxypropyl-2-pyridyl carbinol (XX). This carbinol was catalytically reduced to the corresponding methyl-ω-ethoxypropyl-2-piperidylcarbinol and the latter, on boiling with hydriodic acid, passed partly spontaneously and partly by the subsequent action of sodium ethoxide into β-lupinane (XXI) identical with the product of natural origin.

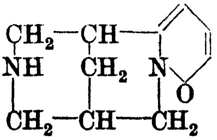

(XVIII.)

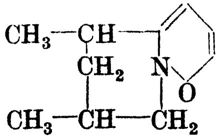

(XIX.)

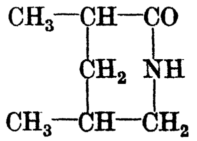

(XX.)


(XXI.)

The relation of lupinine to sparteine and lupanine has been almost completely clarified by a study of cytisine and an allied alkaloidal base, anagyrine, by H. R. Ing. The structure of cytisine is now known with certainty to be (XXII).[16] When it is submitted to exhaustive methylation and degradation under mild conditions so as to prevent polymerisation of the unsaturated *des*-bases, the latter can be reduced and the Hofmann degradation continued in


(XXII.)


(XXIII.)


(XXIV.)

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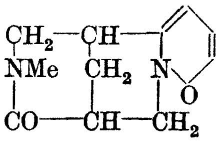
[15] *Ber.*, 1933, **66**, [*B*], 1751.

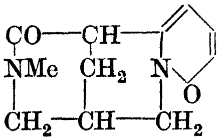
[16] H. R. Ing, *J.*, 1932, 2778; *A.*, 77.

the same way.[17] In this manner a two-stage Hofmann degradation, followed by catalytic reduction of the *des*-bases at each stage, gave a final product, $C_{11}H_{15}ON$, called tetrahydrohemicytisylene (XXIII). On oxidation with ozone this gave a lactam, $C_7H_{13}ON$, which was hydrolysed and oxidised to a mixture of two stereoisomeric αα′-dimethylglutaric acids, $CO_2H{\cdot}CHMe{\cdot}CH_2{\cdot}CHMe{\cdot}CO_2H$, and has accordingly the formula (XXIV). If, however, tetrahydrohemicytisylene (XXIII) is reduced catalytically to octahydrohemicytisylene, this base gives glutaric acid on oxidation. This proves the presence in octahydrohemicytisylene of a chain of three unsubstituted methylene groups. These and other observations can only be reconciled by formula (XXIII) for tetrahydrohemicytisylene, a structure which also accounts for the remarkable production of 6 : 8-dimethylquinoline and the corresponding carbostyril by the action of hydriodic acid and red phosphorus on cytisine.[18]

The constitution of tetrahydrohemicytisylene being regarded as established, it only remains to accommodate an >NH group in its structure to produce cytisine. The final proof of the structure (XXII) for cytisine follows from some observations made by H. R. Ing.[16] *N*-Methylcytisine on oxidation with barium permanganate gives a mixture of two isomeric lactams (XXV) and (XXVI), which can be hydrolysed to amino-acids, and one of these in the form of its benzenesulphonyl derivative loses carbon dioxide at its melting point. Since J. N. Collie[19] found that 6-hydroxy-4-methylpyridine-2-acetic acid lost carbon dioxide at its melting point, the constitution (XXVI) is given to the amide which in subsequent operations loses carbon dioxide.

(XXV.)





(XXVI.)

It is only possible to interpret these results on the structure (XXII) for cytisine. Cytisine in *Anagyris foetida* is accompanied by a second lævorotatory base, anagyrine, $C_{15}H_{20}ON_2$, the formula of which differs from that of cytisine by C_4H_6. This might be accounted for by an additional piperidine or methylpyrrolidine ring in cytisine. H. R. Ing[20] found that anagyrine, on oxidation with barium permanganate, gave only one lactam, anagyramide, $C_{15}H_{18}O_2N_2$, which by the action of ozone gave a new lactam, $C_{11}H_{16}O_2N_2$, with loss of C_4H_2 just as tetrahydrohemicytisylene (XXIII) behaved under the same conditions with loss of a pyridone ring. Since anagyramide loses one molecule of carbon dioxide on treatment with hydriodic acid and phosphorus at 240°, the new carbonyl group is probably β to the pyridone ring as in *N*-methylcytisamide (XXVI). Since anagyrine, unlike cytisine, gives only one amide on oxidation, the most likely point of attachment of the piperidine or methylpyrrolidine ring to cytisine would be as in (XXVII) or (XXVIII).

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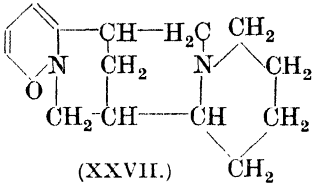
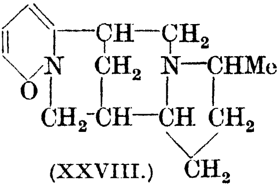
[17] E. Späth and F. Galinowsky, *Ber.*, 1932, **65**, [*B*], 1526; *A.*, 1932, 1146.

[18] M. Freund, *Ber.*, 1904, **37**, 16; *A.*, 1904, i, 263; A. J. Ewins, *J.*, 1913, **103**, 97; E. Späth, *Monatsh.*, 1919, **40**, 15, 93; *A.*, 1919, i, 451, 453.

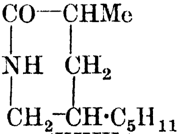
[19] *J.*, 1897, **71**, 299.

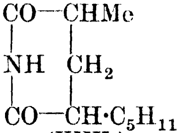
[20] *J.*, 1933, 504; *A.*, 727.

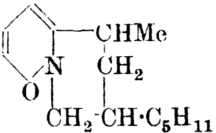

(XXVII.)


(XXVIII.)

When anagyrine was subjected to Hofmann degradation, followed by catalytic reduction at each stage, trimethylamine was eliminated at the third stage: the reduction product, hexahydroanagyryline, $C_{15}H_{23}ON$, lost C_4H_2 on ozonisation to yield a lactam, $C_{11}H_{21}ON$ (XXIX). On hydrolysis and oxidation this lactam gave an oily acid, which yielded a crystalline imide identified as α-methyl-α′-*n*-amylglutarimide (XXX).


(XXIX.)


(XXX.)


(XXXI.)

By analogy with the results obtained by Späth and Galinowsky in the similar degradation of cytisine, hexahydroanagyryline must be represented by (XXXI), and from this it follows that only one position is possible as shown for the methyl group in the pyrrolidine formula (XXVIII). Of the two formulæ (XXVII) and (XXVIII) for anagyrine, the latter is preferred by Ing.

When anagyrine was reduced with hydrogen and palladised charcoal, it was converted into tetrahydroanagyrine; this proved to be identical with *l*-lupanine, which should therefore have the formula (XXXII). When, however, anagyrine was reduced electrolytically, it gave hexahydrodeoxyanagyrine (XXXIII), which proved to be identical with *d*-sparteine. This incidentally was a confirmation of the conversion of *l*-lupanine into *d*-sparteine by G. R. Clemo, R. Raper, and C. R. S. Tenniswood [21] by the action of hydriodic acid and red phosphorus.

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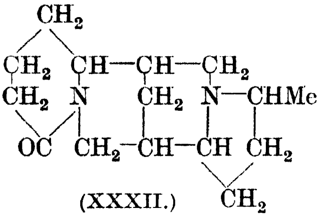
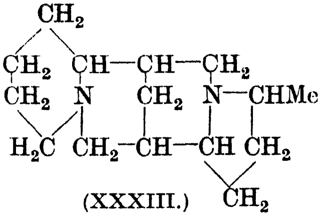
[21] *J.*, 1931, 429; *A.*, 1931, 498.

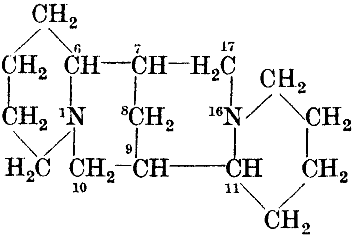


(XXXII.)



(XXXIII.)

Sparteine is known to form two crystalline monomethiodides, but no crystalline dimethiodide is known. Formula (XXXIII) accounts satisfactorily for two structurally different monomethiodides, but it is not immediately obvious why a dimethiodide is not formed. Although C. Moureu and A. Valeur[22] have described an amorphous dimethiodide, G. R. Clemo and R. Raper[23] prefer Ing's alternative structure (XXXIV) for sparteine and account for the absence of a dimethiodide on steric grounds. If the octahydropyridocoline systems are both *trans* and if the C_7–C_9 bridge



(XXXIV.)

is *cis* with respect to the hydrogen atoms attached to C_6 and C_{11}, the system is fairly rigid and the nitrogen atoms are so close to each other that the formation of a dimethiodide is impossible. The formula does not account for two different structural monomethiodides, since such a structure has a diad axis of symmetry. The only alternative appears to be Ing's preferred formula (XXXIII) with the spatial arrangement suggested by Clemo and Raper for the double octahydropyridocoline system. In this case there would be two different structural monomethiodides and no dimethiodide.

The present position is a great step forward, but it cannot be regarded as altogether satisfactory. A critical examination of the results of earlier workers on the breakdown of lupanine and sparteine is now needed in the light of the new formulæ. C. Moureu and A. Valeur[24] have claimed that the difference between the two monomethiodides of sparteine is stereoisomeric and not structural, since they gave among other products the same α-methylsparteine on degradation by Hofmann's method. If Ing's structure (XXXIII) should prove to be correct, this result would seem to indicate a stereochemical change of the nitrogen atom involved, during the preparation of one of the monomethiodides.

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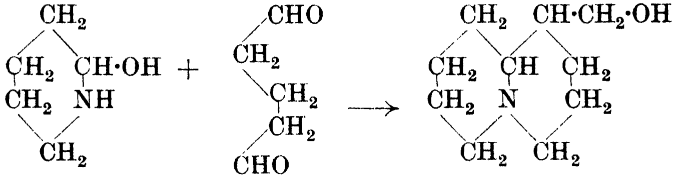
[22] *Bull. Soc. chim.*, 1905, [iii], **33**, 1237.

[23] *J.*, 1933, 644; *A.*, 841.

[24] *Compt. rend.*, 1912, **154**, 312; *A.*, 1912, i, 296.

Sparteine from broom (*Cytisus scoparius*) is lævorotatory, but the *d*-form was obtained from *l*-lupanine by Clemo, Raper, and Tenniswood. *d*-Sparteine has now been found[25] naturally in *Sophora pachycarpa* belonging to the *Leguminosæ* and also in *Thermopsis lanceolata*.[26] In the latter it is accompanied by other bases, among which is thermopsine, $C_{15}H_{20}ON_2$, which on catalytic hydrogenation gives a base, $C_{15}H_{24}ON_2$, isomeric with lupanine and matrine.

Inspection of the formulæ of lupinine, cytisine, anagyrine, lupanine, and sparteine shows that they all contain the lupinine skeleton. R. Robinson[27] has postulated the amino-acid lysine, as did its discoverer Drechsel, as the parent substance of the piperidine group of alkaloids in that it can readily yield a straight chain of five carbon atoms. On this basis C. Schöpf, E. Schmidt, and W. Braun[28] suggest that lupinine arises from two molecules of lysine in the following way :



By extending the scheme to three molecules of lysine, anagyrine, lupanine and sparteine can be readily formulated; cytisine would arise from two molecules of lysine with the intervention of one molecule of formaldehyde.

ψ-Conhydrine. Hemlock (*Conium maculatum*) contains at least five alkaloids, and of these the constitutions of four are known. The last of the five, ψ-conhydrine, $C_8H_{17}ON$, was discovered by Merck in 1891 and its constitution has been determined during the past year by E. Späth, F. Kuffner, and L. Ensfellner.[29] It was known from previous work that ψ-conhydrine was probably a hydroxyconiine, and the position of the hydroxyl group has now been settled by a Hofmann degradation. The product of the first stage of the degradation on catalytic reduction gave dihydro-ψ-conhydrinemethine, $C_{10}H_{23}ON$, which on oxidation with permanganate gave *n*-heptoic acid, identified as its phenylhydrazide. This limits the possible positions of the hydroxyl group in the coniine molecule to two, (XXXV) and (XXXVI). The former is

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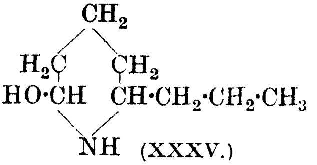
[25] A. Orekhov, M. Rabinovitsch, and R. Konovalova, *Ber.*, 1933, **66**, [*B*], 621; *A.*, 617.

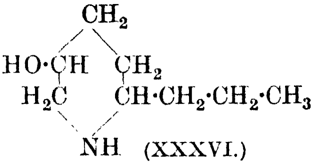
[26] A. Orekhov, S. Norkina, and H. Gurevitsch, *ibid.*, p. 625; *A.*, 617.

[27] *J.*, 1917, **111**, 882; *A.*, 1917, i, 664.

[28] *Ber.*, 1931, **64**, [*B*], 683; *A.*, 1931, 635.

[29] *Ibid.*, 1933, **66**, [*B*], 591; *A.*, 516.

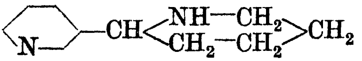

(XXXV.)

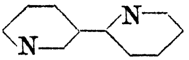

(XXXVI.)

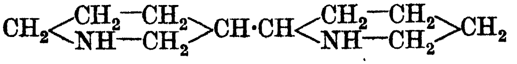
excluded because dihydro-ψ-conhydrinemethine would be represented as an additive compound of *n*-octaldehyde and dimethylamine and as such would be unstable to acids. ψ-Conhydrine must accordingly be represented by (XXXVI).

Pyridine Group.—*Anabasis aphylla*, a Central Asian plant of the natural order *Chenopodiaceæ*, has been examined by A. Orekhov and G. Menschikov [30] on account of its reputed toxic qualities. It contains 2% of alkaloidal bases, which have been fractionated by various means into a low-boiling fraction containing crystalline lupinine and a liquid, anabasine, an isomeride of nicotine, and a high-boiling fraction containing at least three crystalline alkaloids: aphylline, $C_{15}H_{24}ON_2$, isomeric with lupinane and matrine, aphyllidine, $C_{15}H_{22}ON_2$, and a base, possibly $C_{16}H_{26}O_2N_2$. This appears to be the first record of alkaloids occurring in the *Chenopodiaceæ* and it is of interest though not novel that lupinine previously found in *Papilionaceæ* should occur in plants belonging to different families.

Anabasine is optically active and on oxidation with permanganate gives nicotinic acid. When dehydrogenated with silver acetate or by boiling with zinc dust, it gives 2 : 3′-dipyridyl (II) identical with the synthetic material.[31] Anabasine is therefore *l*-3-(2′-piperidyl)pyridine (I). The possibility of ring enlargement from a methylpyrrolidine seems to be excluded, since M. Ehrenstein [32]

(I.)



(II.)


$CH_2{<}\begin{matrix}CH_2-CH_2\\NH-CH_2\end{matrix}{>}CH\cdot CH{<}\begin{matrix}CH_2-CH_2\\NH-CH_2\end{matrix}{>}CH_2$ (III.)

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[30] *Ber.*, 1931, **64**, [*B*], 266; *A.*, 1931, 498.

[31] A. Orekhov and G. Menschikov, *ibid.*, 1932, **65**, [*B*], 232; *A.*, 1932, 405.

[32] *Ibid.*, 1931, **64**, [*B*], 1137; *A.*, 1931, 850.

has shown that by catalytic dehydrogenation of *N*-methylated and *C*-methylated pyrrolidines by means of platinised asbestos no ring enlargement occurs. On reduction of anabasine by sodium and alcohol or catalytically in the presence of Adams's platinum oxide it yields a mixture of bases, from which an *l*-2 : 3′-dipiperidyl (III) has been isolated.

In a search for insecticides, C. R. Smith[33] found that when sodium dipyridyl is digested with excess of pyridine and then oxygen passed through the solution a mixture of 2 : 2′-, 3 : 3′-, 3 : 4′-, and 4 : 4′-dipyridyls is formed. The pure bases were relatively non-toxic to plant lice, but the crude mixture was toxic. On further examination of the mixture of bases[34] 3-(2′-piperidyl)-pyridine has been isolated : it is named neonicotine on account of its relation to nicotine and its toxicity to aphids and other soft-bodied insects. It has been shown to be the racemic form[35] of anabasine, isolated from anabasine sulphate, which, as an insecticide, is now an article of commerce. Both Smith and Orekhov are agreed that anabasine is not identical with A. Pictet and A. Rotschy's subsidiary alkaloid nicotimine[36] obtained from tobacco, to which the constitution of 3-(2′-piperidyl)pyridine was assigned. M. Ehrenstein[37] has, however, shown by fractional distillation of the bases and fractionation of the picrates that "nicoteine" from Kentucky tobacco is a mixture of nornicotine and anabasine.

It is convenient to record here the noteworthy experiments of G. T. Morgan and F. H. Burstall[38] on the dehydrogenation of pyridine on the large scale at 340° and 50 atmospheres pressure by means of anhydrous ferric chloride. 2 : 2′-Dipyridyl was the main product and no fewer than twenty other by-products were isolated, including 2 : 3′-dipyridyl, the dehydrogenation product of anabasine.

The other alkaloids, aphylline and aphyllidine, obtained by Orekhov and Menschikov[31] were subjected to exhaustive methylation and degradation. Trimethylamine was liberated in each case after three repetitions of the Hofmann reaction, so the basic nitrogen atom of aphylline and aphyllidine is dicyclic like the nitrogen atoms in sparteine and lupinine.

A new synthesis of nornicotine has been described during the past year.[39] Nicotinonitrile and the Grignard reagent prepared from ethyl γ-bromopropyl ether gave 3-pyridyl γ-ethoxypropyl ketone (IV), which formed an oxime (V) reducible to α-amino-δ-ethoxy-α-3-pyridylbutane. The latter base, when heated with 48%

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[33] *J. Amer. Chem. Soc.*, 1924, **46**, 414; *A.*, 1924, i, 558.

[34] *Ibid.*, 1931, **53**, [*B*], 277; *A.*, 1931, 367.

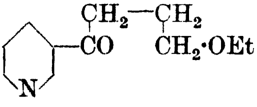
[35] *Ibid.*, 1932, **54**, [*B*], 397; *A.*, 1932, 287.

[36] *Ber.*, 1904, **37**, 1225; *A.*, 1904, i, 520.

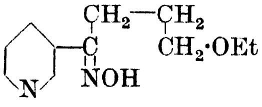
[37] *Arch. Pharm.*, 1931, **269**, 627; *A.*, 1931, 177.

[38] *J.*, 1932, 20; *A.*, 1932, 284.

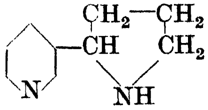
[39] L. C. Craig, *J. Amer. Chem. Soc.*, 1933, **55**, 2854; *A.*, 960.



(IV.)



(V.)

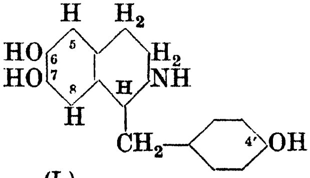


(VI.)

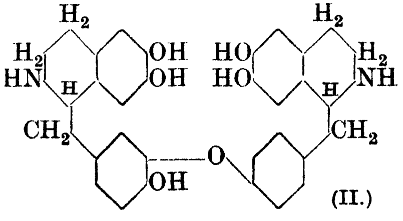
hydrobromic acid, gave nornicotine (VI) with properties agreeing with those given by J. v. Braun and K. Weissbach [40] for nornicotine prepared from natural nicotine.

*Bisbenzyl*iso*quinoline Group.*—The *iso*quinoline group of alkaloids is a very extensive one, embracing as it does the papaverine group, the berberine or di*iso*quinoline group, the phenanthripyridine group, and the morphine group. Each of these may be regarded as containing in its structure a benzyl*iso*quinoline nucleus. The constitutions of so many representatives of these four groups have been worked out that the subject has almost lost the elements of surprise and novelty. Almost the sole exception is the papaverine group, which in a subdivision contains a number of alkaloids classified as the bisbenzyl*iso*quinoline group to distinguish them from those of the di*iso*quinoline (berberine) group. As the name suggests, they contain two separate benzyl*iso*quinoline structures, and these are joined by ether linkages. Without committing ourselves as to its phytogenetic origin, we may, following F. Faltis,[41] regard the ether linkage for purposes of exposition and classification as having arisen by a process of dehydrogenation between a hydroxyl group and a nuclear hydrogen atom.

This class of alkaloids is coming into prominence through the discovery, first made by E. Späth and A. Kolbe [42] in the case of oxyacanthine, that certain alkaloids heretofore regarded as simple benzyl*iso*quinolines contain in reality two such structures.



(I.)



(II.)

Norcoclaurine (I) will serve to illustrate some of the possibilities of ether formation. The simplest case is shown in (II) where ether formation has taken place between the 4′-hydroxyl of one molecule and a nuclear hydrogen atom ortho to the 4′-hydroxyl of a second molecule. Such a case is of a type possibly found in the alkaloid dauricine. If, in addition, ether formation takes place between a phenolic group of one *iso*quinoline nucleus and a nuclear hydrogen atom of the second *iso*quinoline nucleus as in (III), alkaloids of the type of oxyacanthine, tetrandrine, and berbamine are formed.

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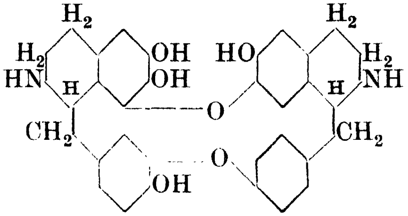
[40] *Ber.*, 1930, **63**, [*B*], 2018; *A.*, 1930, 1444.

[41] *Ibid.*, p. 809; *A.*, 1930, 774.

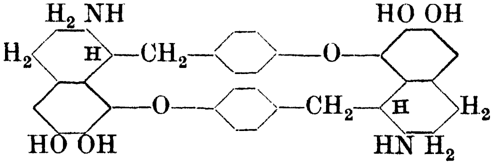
[42] *Ibid.*, 1925, **58**, 2282; *A.*, 1926, 82.



(III.)

The benzyl*iso*quinoline nuclei could, however, combine to form a symmetrical type (IV) and it is probable that *iso*chondodendrine belongs to this class. Various other types are possible, but only one other has been encountered, namely, a structure containing three ether linkages; such occurs in trilobine, *iso*trilobine, and probably phæanthine.

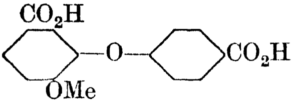
(IV.)

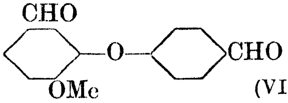


Completely methylated structures of each of these types will undergo Hofmann degradation in the usual way with the formation of methines in which the carbon atoms adjacent to the nitrogen atoms lose their asymmetry. In the case of phæanthine and *iso*chondodendrine, for instance, an optically active methine accompanies the inactive one and the occurrence of optical activity is naturally attributed to fission of the heterocyclic nitrogen-containing ring on the side of the nitrogen atom remote from the asymmetric centre and the benzyl group. The methines derived from structures (II) and (III) will give nitrogen-free dicarboxydiphenyl ethers on oxidation, whilst oxidation of the vinyl compounds formed by a two-stage Hofmann degradation will give valuable information about the structure of the *iso*quinoline nuclei. At the present time it cannot be said that any single alkaloid belonging to these types has had its structure elucidated beyond all shadow of doubt, but the results so far obtained merit discussion.

Of the dozen or so alkaloids which have been examined in this group it is of interest that at least six give, by the Hofmann degradation, methines which on oxidation yield one and the same 2-methoxy-5 : 4′-dicarboxydiphenyl ether (VI). The alkaloids

(VI.)

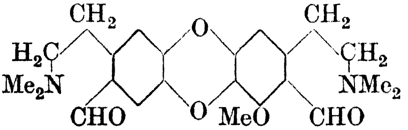




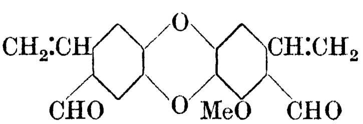
(VII.)

which behave thus are tetrandrine, trilobine, *iso*trilobine, berbamine, trilobamine, and phæanthine. The methoxy-group in (VI) is present in the alkaloids oxyacanthine and dauricine as a phenolic group, since on ethylation of these alkaloids and degradation, the above acid (VI) is replaced by the corresponding ethoxy-derivative. The differences between these eight alkaloids must therefore reside mainly in the mode of substitution and attachment of groups in the *iso*quinoline nuclei.

Trilobine and *iso*trilobine (formerly homotrilobine) occur in *Cocculus trilobus* and *C. sarmentosus* and are isomeric.[43] On oxidation of the methines with ozone they both yield the dialdehyde (VII), for on oxidation it gives the acid (VI). The nitrogenous half of the molecule appears as (VIII), which by Hofmann degradation gives the *o*-divinyldialdehyde (IX). This dialdehyde is

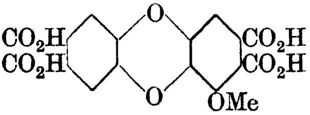


(VIII.)

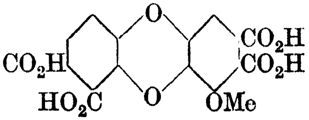


(IX.)

oxidised by permanganate to a tetracarboxylic acid (X), for by alkali fusion it yields protocatechuic acid and probably a trace of gallic acid as is shown by the ferric chloride reaction. The divinyldialdehyde (IX) forms an anil; this combines with methyl



(X.)



(XI.)

iodide to give a substance which on digestion with dilute mineral acid yields a small quantity of a phenolic product. Since, of the three methoxybenzaldehydes, only the *o*-derivative under similar conditions loses its methyl group,[44] the methoxy-group in (IX) must probably occupy the position shown next to the aldehyde group. The position assigned to the ether linkages is the most probable on general grounds but will need substantiation by synthesis. Since trilobine and *iso*trilobine are isomeric but yield the same products of fission, their constitutions are probably represented by (XII) and (XIII).

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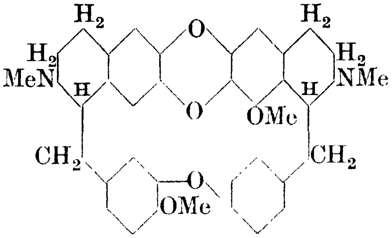
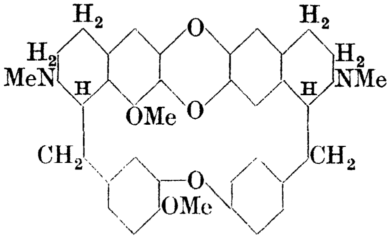
[43] H. Kondo and M. Tomita, *Annalen*, 1932, **497**, 104; *A.*, 1932, 1048.

[44] M. Freund and F. Becker, *Ber.*, 1903, **36**, 1521; *A.*, 1903, i, 572.



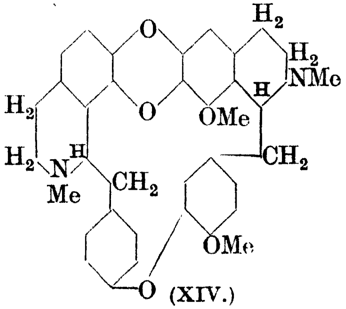
(XII.)



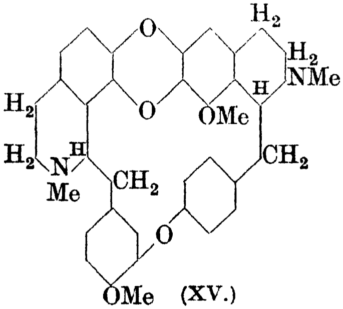
(XIII.)

The positions of the oxygen atoms in the two *iso*quinoline nuclei are in agreement with the position in *iso*quinoline alkaloids of well-substantiated structure such as laudanosine and narcotine. On biogenetic grounds these structures, if substantiated, are of special interest, since, whatever view is adopted as to the mode of formation of the ether linkages between the *iso*quinoline nuclei —dehydrogenation as postulated by Faltis or anhydride formation between hydroxyl groups—the units concerned must have been different.

Alternative structures (XIV) and (XV) have, however, been advanced by F. Faltis[45] which would fit the experimental facts so far recorded. The acid obtained by degradation of the *iso*quinoline nuclei would, however, have the structure (XI) and not (X) as is demanded by Kondo and Tomita's arrangement.



(XIV.)



(XV.)

It is probable that phæanthine, an alkaloid obtained by A. C. Santos[46] from *Phœanthus ebracteolatus* of the natural order *Anonaceæ* and related to the order *Menispermaceæ*, belongs to the same type as trilobine and *iso*trilobine. On oxidation of its optically inactive methine it gives the same 2-methoxy-5 : 4′-dicarboxydiphenyl ether (VI) as these two alkaloids and the formula proposed by Santos on the basis of its reactions is shown in (XVI). F. Faltis, S. Wrann, and E. Kühas [47] regard (XVII) as the only possible formula for phæanthine which would be free from strain and

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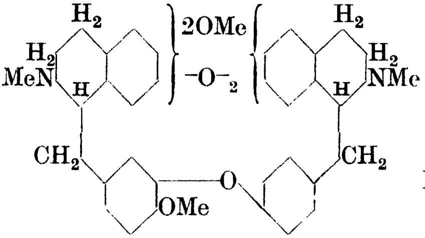
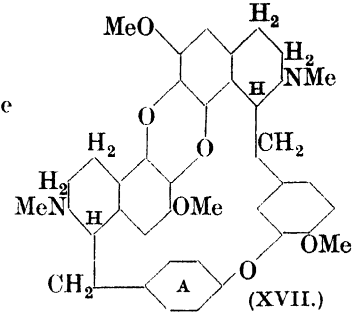
[45] *Annalen*, 1932, **499**, 301.

[46] *Ber.*, 1932, **65**, [*B*], 472; *A.*, 1932, 527.



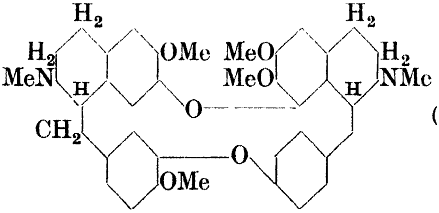
(XVI.)



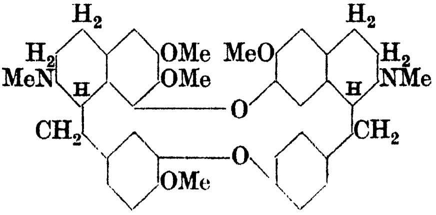
(XVII.)

would give an optically inactive methine. The plane of the ring A is perpendicular to the rest of the molecule and to the plane of the paper and free rotation of A is not possible owing to obstruction. When the two asymmetric centres are destroyed by degradation to the methines, optical activity is lost, since the plane of the paper is a plane of symmetry. Formula (XVII) is attractive biogenetically, since it could arise by dehydrogenation of two molecules of norcoclaurine (I) and subsequent methylation.

Through the combined efforts of several groups of workers the constitutions of the alkaloids tetrandrine, berbamine *O*-methyl ether, and oxyacanthine *O*-methyl ether are now known to be represented by the structure (XVIII) or (XIX), finally suggested



(XVIII.)



(XIX.)

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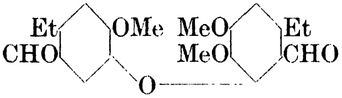
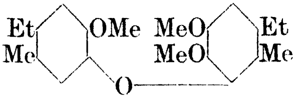
[47] *Annalen*, 1932, **497**, 76; *A.*, **1932**, 1047.

by F. v. Bruchhausen, H. Oberembt, and A. Feldhaus.[48] For much of our knowledge of the constitution of oxyacanthine we are indebted to E. Späth and to F. v. Bruchhausen and their collaborators.[49] H. Kondo and Y. Yano[50] have shown that tetrandrine, an alkaloid from *Stephania tetrandra*, and oxyacanthine *O*-methyl ether prepared from *Berberis Thumbergii* both give the same series of products on degradation and oxidation after exhaustive methylation. Furthermore, berbamine, an alkaloid discovered originally by O. Hesse in *Berberis vulgaris* and found also in *Berberis Thumbergii* by H. Kondo and M. Tomita,[51] has been shown by A. C. Santos[52] to be isomeric with oxyacanthine and to give on oxidation the same 2-methoxy-5 : 4′-dicarboxydiphenyl ether (VI) as is obtained from oxyacanthine *O*-methyl ether and from tetrandrine. The constitution of the *iso*quinoline portions of these alkaloids has been clearly solved by F. v. Bruchhausen, Oberembt, and Feldhaus.[48] After a two-stage Hofmann degradation of oxyacanthine *O*-methyl ether, a dialdehyde (XX) was obtained which was reduced by Clemmensen's method to a trimethoxydimethyldiethyldiphenyl ether (XXI). This ether proved to be identical with a synthetic product obtained by an Ullmann condensation on appropriate products.



(XX.)



(XXI.)

Since tetrandrine, oxyacanthine *O*-methyl ether, and berbamine *O*-methyl ether give exactly the same oxidation products after exhaustive methylation and degradation, their structure must be represented by (XVIII) or (XIX). One of these formulæ must be given to tetrandrine and to berbamine *O*-methyl ether, since, after the first stage of the Hofmann degradation where the two asymmetric centres are lost, the inactive methines produced are identical. From the magnitude of the specific rotations it is probable that in tetrandrine the two asymmetric centres each contribute a dextrorotation, whilst in berbamine *O*-methyl ether one contributes a dextro- and the other a lævo-rotation. The other formula must be assigned to oxyacanthine *O*-methyl ether, since its methine is different.

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[48] *Annalen*, 1933, **507**, 144; *A.*, 1313. Compare F. v. Bruchhausen and P. H. Gericke, *Arch. Pharm.*, 1931, **269**, 115; *A.*, 1931, 636.

[49] E. Späth and A. Kolbe, *Ber.*, 1925, **58**, 2280; *A.*, 1926, 82; E. Späth and J. Pikl, *ibid.*, 1929, **62**, 2251; *A.*, 1929, 1319; F. v. Bruchhausen and H. Scholtze, *Arch. Pharm.*, 1929, **267**, 617; *A.*, 1930, 98.

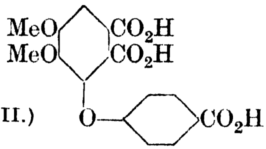
[50] *Annalen*, 1932, **497**, 90; *A.*, 1932, 1048.

[51] *J. Pharm. Soc. Japan*, 1930, **50**, 309.

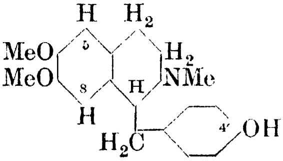
[52] *Dissert.*, Munster, 1929.

It is probable that menisarine, an alkaloid found by H. Kondo and M. Tomita [53] in *Cocculus saramentosus*, and trilobamine from *C. trilobus* [54] also possess the same type of alkaloidal structure.

The problem of the constitution of *iso*chondodendrine presents some interesting features. *O*-Methyl*iso*chondodendrine was originally thought by Faltis and his associates [55] to be $C_{19}H_{21}O_3N$, since Rast's camphor method gave rather high molecular weights for this formula but very low values for a double structure, but recent work [47] has shown that the molecular weight in suitable solvents is just double. On two-stage Hofmann degradation and oxidation methyl*iso*chondodendrine gives 2 : 3-dimethoxy-5 : 6 : 4′-tricarboxydiphenyl ether (XXII) as the only well-characterised product, the constitution of which has been established by synthesis.[47]

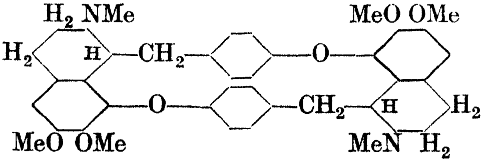


(XXII.)

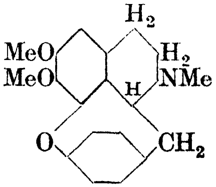


(XXIII.)

It is clear that such a structure could arise exclusively in a Hofmann oxidative degradation from an alkaloid based on the structure (XXIII) only if ether formation between two such molecules had taken place between each 4′-hydroxyl and the hydrogen atom in position 5 or 8 of the other molecule. In the latter case the resultant structure would be (XXIV).



(XXIV.)



(XXV.)

If the two components of this structure based on (XXIII) were both dextro- or both lævo-modifications, the resulting structure (XXIV) would be optically active; but if the components were severally dextro- and lævo-rotatory, the resulting structure would be optically inactive and would be centro-symmetrical. A study of models shows that in (XXIV) we have a very compact three-dimensional structure in which the plane of the phenyl nuclei of the benzyl groups is approximately perpendicular to the plane of the *iso*quinoline nuclei. Even in the methine bases free rotation of these phenyl nuclei is said not to be possible, but whatever the optical sign of the components on which the structure is built, the methines will be inactive through centro-symmetry.[47]

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[53] *J. Pharm. Soc. Japan*, 1930, **50**, 633; *A.*, 1931, 243.
[54] *Idem, ibid.*, 1931, **51**, 452.
[55] F. Faltis and F. Neumann, *Monatsh.*, 1921, **42**, 311; *A.*, 1922, i, 569.

The same would apply to a structure formed by ether linkages between the 4′-hydroxyl groups and the 5-hydrogen atoms of parallel molecules of (XXIII), but if the ether linkages were formed between the 4-hydroxyl of one molecule and the 5-hydrogen atom of the second molecule and between the 4′-hydroxyl of the second molecule and the 8-hydrogen atom of the first, then the methines should be optically active, since they would be very compact three-dimensional structures without a plane or centre of symmetry.

Actually, methyl*iso*chondodendrine is optically active but gives an inactive methine. Its most probable formula is that shown in (XXIV).

E. Späth, W. Leithe, and F. Ladeck [56] have shown that *l*-curine from tubocurare is the optical enantiomorph of *d*-bebeerine (α-chondodendrine), an alkaloid obtained from Pareira root by M. Scholtz,[57] and on the basis of their reactions have suggested the formula (XXV) for the methyl ether. Since the molecular weight as determined by Rast's method is abnormally high for this simple structure, which on steric grounds is already improbable, it seems likely that curine has double the formula hitherto attributed to it. Its structure would probably have to be based on (XXIV).*

The remaining alkaloid for consideration in this group is dauricine, obtained by H. Kondo and S. Narita [58] from *Menispermum dauricum*. Determination of the molecular weight by Rast's method in camphor gave results in agreement with the formula $C_{19}H_{23}O_3N$, but oxidation of dauricine *O*-methyl ether after it had been subjected to a two-stage Hofmann degradation and had thus yielded a nitrogen-free substance gave *m*-hemipinic acid (3 : 4-dimethoxyphthalic acid) and 2-methoxy-5 : 4′-dicarboxydiphenyl ether (VI). F. Faltis and H. Frauendorfer [59] have suggested the structure (XXVI) for dauricine, but the Japanese observers reaffirm the simple molecular weight as determined by Rast's method and adhere to the formula (XXVII). In view of the difficulty of reconciling the latter structure with the oxidation products of the degraded *O*-methyl ether, Faltis, Wrann,

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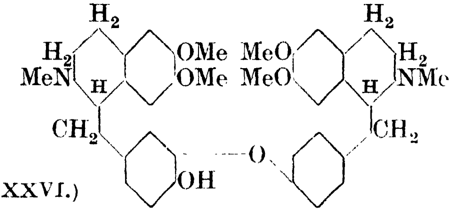
[56] *Ber.*, 1928, **61**, 1705; *A.*, 1928, 1264.

[57] *Arch. Pharm.*, 1906, **244**, 555; *A.*, 1907, i, 79.

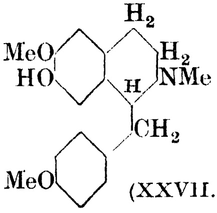
[58] *J. Pharm. Soc. Japan*, 1927, **542**, 40.

[59] *Ber.*, 1930, **63**, [*B*], 809; *A.*, 1930, 774.

* Since the above was written a solution in this sense has been advanced by E. Späth and F. Kuffner (*Ber.*, 1934, **67**, [*B*], 55).



(XXVI.)



(XXVII.)

and Kühas[47] express the belief that dissociation of the structure (XXVI) takes place in camphor at the ether linkage and this would account for the low molecular weight found by the Japanese observers.

Pyrrole Pigments.

The fundamental importance of the pyrrole nucleus in some of the major chemical problems of the day needs no emphasis. It is perhaps not generally realised that the only enzymes whose chemical nature is known are derivatives of the porphyrins. The reducing enzyme chlorophyll, the constitution of which is nearing an agreed solution through the labours of Willstätter, Hans Fischer, Conant, and Stoll, is a magnesium porphyrin, and certain enzymes concerned with oxidative processes are iron porphyrins, *e.g.*, catalase,[60] peroxidase,[61] and the respiratory ferment.[62] Quite recently it has been shown by K. Zeile and F. Reuter[63] that Keilin's respiratory pigment cytochrome *c* yields on treatment with hydrobromic acid in acetic acid, followed by hydriodic acid, crystalline mesoporphyrin which was found through its methyl ester to be identical with mesoporphyrin obtained from the hæmin of blood. This confirms an earlier observation of R. Hill and D. Keilin,[64] who, by the action of hydrobromic acid in acetic acid on cytochrome *c* preparations, obtained a solution of hæmatoporphyrin identical in physical properties with the natural product.

It is truer than ever it was that the discoveries of the biochemist to-day are to-morrow the problems of the organic chemist. This is notably so in the group of pyrrole pigments. Prodigiosin, the red pigment of *Bacillus prodigiosus*, contains two or three pyrrole nuclei.[65] Lanaurin, an amorphous pigment isolated from the wool of sheep exhibiting a golden colour, is related to bilirubin,[66] and from the bile of certain light-sensitive sheep C. Rimington and J. I. Quin [67] have isolated crystalline phylloerythrin, a metabolic product of chlorophyll. Quite recently a preliminary announcement has appeared that the colouring matter, bacteriochlorophyll, of the sulphur-free purple bacteria is closely related to chlorophyll. It contains magnesium and yields a bacteriophæophytin with a spectrum similar to that of phæophytin. On treatment with hydrogen iodide and acetic acid it gives a porphyrin mixture very similar in spectral behaviour to phylloerythrin.[68]

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[60] K. Zeile and H. Hellström, *Z. physiol. Chem.*, 1930, **192**, 17; *A.*, 1931, 123.

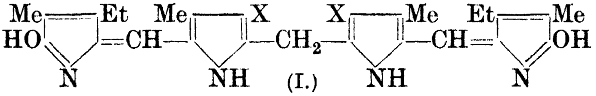
[61] R. Kuhn, D. B. Hand, and M. Florkin, *ibid.*, 1931, **201**, 255; *A.*, 1931, 1455.

[62] O. Warburg and E. Negelein, *Biochem. Z.*, 1929, **214**, 64; *A.*, 1929, 1475.

[63] *Z. physiol. Chem.*, 1933, **221**, 101; *A.*, 1934, 109.

[64] *Proc. Roy. Soc.*, 1930, [*B*], **107**, 286; *A.*, 1931, 125.

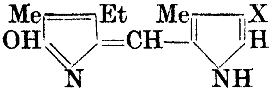
In last year's *Report* the synthesis of mesobilirubin (I) was described ($X = \cdot CH_2\cdot CH_2\cdot CO_2H$). It showed a very close similarity



(I.)

to mesobilirubin prepared by catalytic reduction of natural bilirubin, the pigment of the bile. On the other hand it contained an orientation of groups in the β-positions in the pyrrole nuclei corresponding to ætioporphyrin (IV),[69] which has no known natural representative. Such a structure would also imply that conversion of blood pigments into bilirubin involves intermediate degradation to pyrrole units and then re-synthesis, a probability which seems rather remote. However, further work [70] has elucidated a great deal.

When mesobilirubin (I) was fused with resorcinol it gave a neoxanthobilirubic acid (II) melting 13° higher than neoxanthobilirubic acid prepared from mesobilirubin from natural sources. A new confirmatory synthesis of neoxanthobilirubic acid (II) was then effected : 5-bromo-2-formyl-4-methyl-3-ethylpyrrole (III) was



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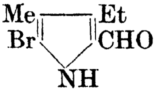

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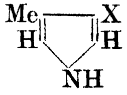

(IV.)

condensed with opsopyrrolecarboxylic acid (IV) with the aid of hydrobromic acid to 5-bromo-4 : 3′-dimethyl-3-ethylpyrromethene-

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[65] F. Wrede and A. Rothhaas, *Z. physiol. Chem.*, 1933, **215**, 67; *A.*, 516; H. Raudnitz, *Naturwiss.*, 1933, **21**, 518; *A.*, 959.

[66] C. Rimington and A. M. Stewart, *Proc. Roy. Soc.*, 1932, [*B*], **110**, 75; *A.*, 1932, 417.

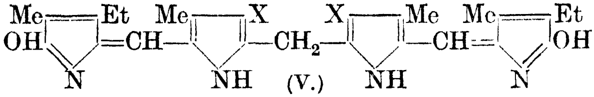
[67] *Nature*, 1933, **132**, 178.

[68] K. Noack and E. Schneider, *Naturwiss.*, 1933, **47**, 835.

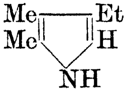
[69] *Ann. Reports*, 1932, 216.

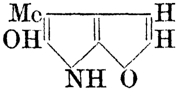
[70] W. Siedel and H. Fischer, *Z. physiol. Chem.*, 1933, **214**, 145; *A.*, 404.

4′-propionic acid (II, OH replaced by Br), which on treatment with sodium methoxide and a little water at 150° gave neoxanthobilirubic acid (II). These synthetic neoxanthobilirubic acids were identical; they had higher melting points than that from natural sources, but showed no depression in admixture; a similar behaviour was shown by derivatives. These results made it extremely probable that mesobilirubin from natural sources must have an orientation of β-substituents not as in (I) but as in hæmin and shown in (V). Such a view would also explain the origin of hæmopyrrole (VI)


(V.)

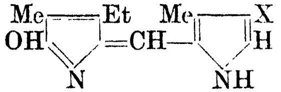
obtained by the action of hydriodic acid on bilirubin and of the pyrrofuran (VII) obtained in small yield by the action of nitrous

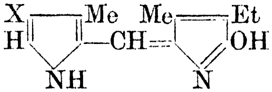
(VI.)



(VII.)

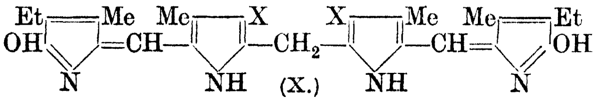
acid, which were difficult to reconcile with an orientation of groups based on (I).

When mesobilirubin from natural sources was re-examined by the resorcinol-melt method the product was found to be a mixture of two isomeric acids (VIII) and (IX) partly separable by means of their methyl esters.

(VIII.)



(IX.)

The second acid (IX), now called *iso*neoxanthobilirubic acid, was a new acid, its constitution being proved by its synthesis by a resorcinol-melt of a synthetic symmetrical mesobilirubin of the following formula [71] (X).


(X.)

Many slight discrepancies in melting points and properties between the synthetic and the natural products thus received clarification and bilirubin (XI) becomes naturally a biological oxidation product of hæmin by scission of an α-methine bridge with formation of two α-hydroxyl groups. The synthesis of mesobilirubin (V) and of bilirubin (XI) will be the final confirmation of the correctness of these views.

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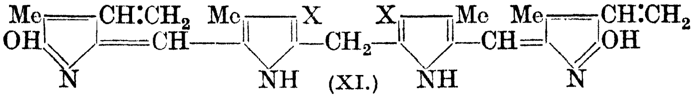
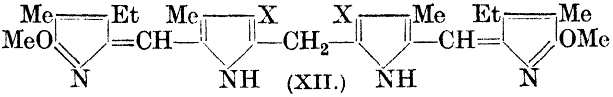
[71] H. Fischer and E. Adler, *Z. physiol. Chem.*, 1931, **200**, 227; *A.*, 1931, 1420.

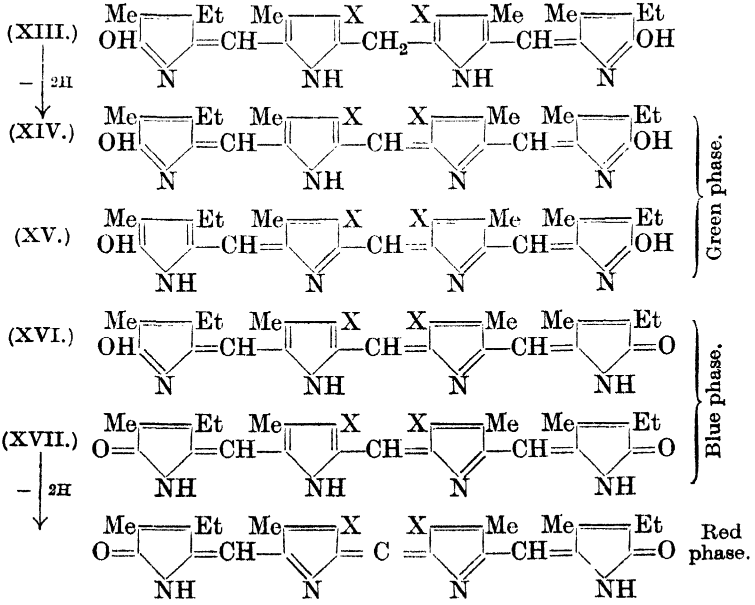
When bilirubin in chloroform is carefully treated with nitric acid containing nitrite, the chloroform solution passes through a series


(XI.)

of colour changes from green, violet, and red to yellow (Gmelin's reaction). The *O*-methyl ether of neoxanthobilirubic acid (II) on condensation with formaldehyde and hydrochloric acid gives a symmetrical dimethyl ether of mesobilirubin (XII) the colour change of which under the conditions of the Gmelin reaction stops


(XII.)

at the green phase. The Gmelin reaction has been previously interpreted as a series of oxidative steps ending in a holoquinonoid type [72] and since the above dimethyl ether cannot pass into a substance of quinonoid type, the green phase cannot involve such a change. The steps in the reaction have now been formulated in the following way : [73]



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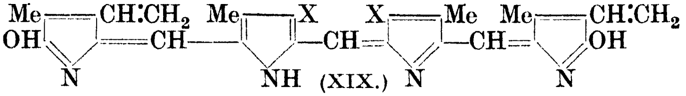
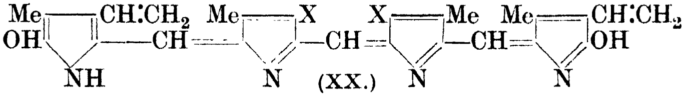
[72] H. Fischer and E. Adler, *Z. physiol. Chem.*, 1932, **206**, 187 ; *A.*, 1932, 627.

[73] H. Fischer and W. Siedel, *ibid.*, 1933, **214**, 145 ; *A.*, 404.

Such a scheme, if correct, will prove of great value in elucidating the exact arrangement to be attributed to the variety of coloured natural pigments in this group. Glaucobilin, obtained by the action of ferric chloride, followed by alkali, on mesobilirubin, is blue [74] and should contain a quinone type (XVI) or (XVII) in its structure; R. Lemberg,[75] however, for other reasons regards it as belonging to the green phase of the Gmelin reaction. The strikingly green uteroverdin obtained from the dog's placenta by Lemberg should be formulated as (XIX) or (XX).



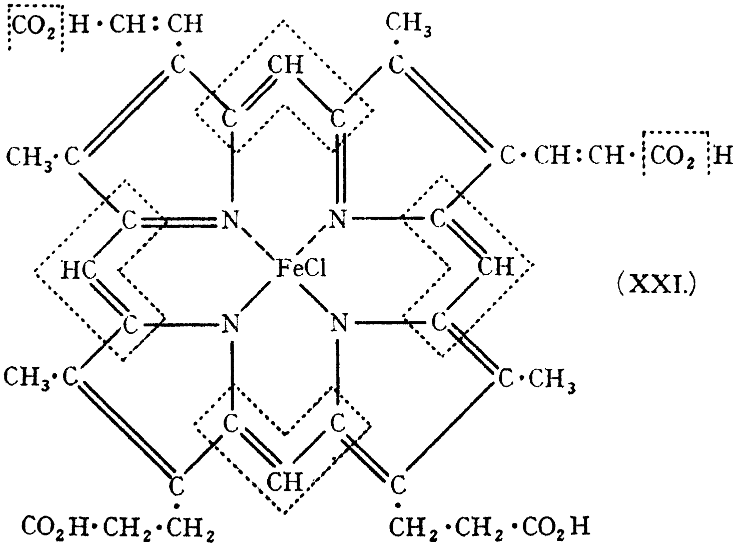
(XIX.)



(XX.)

The pigment of seagulls' eggs has been identified with uteroverdin by Lemberg, but there are slight differences which might be explicable by formulæ such as (XIX) and (XX).

Some recent observations of Lemberg [75] on the chromoproteins of red algæ or sea-weeds, particularly Japanese Nori, are of great interest. Two chromoproteins, phycocyan and phycoerythrin,



(XXI.)

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[74] H. Fischer, H. Baumgartner, and R. Hess, *Z. physiol. Chem.*, 1932, **206**, 201; *A.*, 1932, 627.

[75] *Annalen*, 1933, **505**, 160; *A.*, 1060.

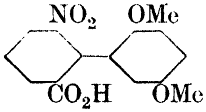
both give on boiling with 10% methyl-alcoholic potash dehydromesobilirubin (glaucobilin), and phycoerythrin also gives a small proportion of mesobilirubin. If these structures are present in the original pigments, the absence of vinyl groups in the β-position shows that they belong to the chlorophyll group rather than to the hæmin group of pigments.

The biogenesis of the blood-pigments is a highly speculative subject without any direct experimental evidence bearing upon it. On the basis of the constitution of hæmin proved by H. Fischer's synthesis, H. Emde[76] has put forward an arrangement (XXI) whereby hæmin is formed from four normal C_6 chains and four C_3 chains or six molecules of a monose in all, the vinyl groups arising by loss of carbon dioxide from the unsaturated side chains.

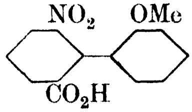
A somewhat similar scheme advanced by R. Robinson[77] is not reproduced here, since it was based on the now discarded Willstätter formula for the porphyrins with a central ethylene bridge.

Optical Activity.

Dissymmetry due to Restricted Rotation.[78]—The diphenyl field is an inexhaustible store of interesting problems and as such attracts the attention of numerous workers. A survey of the extensive literature shows that all cases of resolution in diphenyl and allied derivatives confirm the theory of mechanical hindrance to free rotation of the opposing nuclei produced by substituents in the ortho-positions. Much of the recent work has centred round the determination of the smallest atoms or groups which will hinder rotation. H. C. Yuan and R. Adams[79] combined 2′-nitro-2 : 5-dimethoxydiphenyl-6′-carboxylic acid (I) with brucine, and isolated almost all of it as the salt with the *l*-acid, the *d*-acid passing into the *l*-acid as the latter was removed from the solution as the least sparingly soluble salt with brucine. This salt, however, was unstable in chloroform solution and rapidly racemised. The free *l*-acid racemised completely in organic solvents at room temperature in 60—70 minutes. The methoxy-group has therefore little obstructing



(I.)



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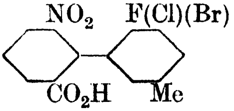

(III.)

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[76] *Pharm. Acta Helv.*, 1929, **8**, 121.

[77] *Proc. Univ. Durham Phil. Soc.*, 1927, **8**, 14.

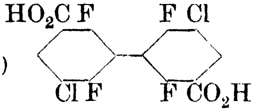
[78] A useful summary by R. Adams and H. C. Yuan is to be found in *Chem. Reviews*, 1933, **12**, 261.

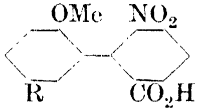
[79] *J. Amer. Chem. Soc.*, 1932, **54**, 2966; *A.*, 1932, 945.

power. This was confirmed in 2-nitro-2′-methoxydiphenyl-6-carboxylic acid (II); this also only gave one alkaloidal salt, which showed mutarotation.[80] The three acids shown in (III) were prepared and submitted to resolution. 2′-Chloro- and 2′-bromo-2-nitro-5′-methyldiphenyl-6-carboxylic acids were obtained in *d*- and *l*-forms which were only slowly racemised, the chloro-acid more readily than the bromo-acid, but the 2-fluoro-derivative could only be isolated in one form, which as a brucine salt racemised rapidly at 0° in chloroform. The relative interference effects on nuclear rotation are therefore in the order Br>Cl>MeO>F, which is the order to be expected from the relative diameters of the elements concerned.

Since, next to hydrogen, oxygen and fluorine are the atoms of smallest atomic radius which can be used as substituents, considerable attention has been paid by Adams and his co-workers to diphenyl derivatives containing methoxy- and fluoro-groups in the ortho-positions, and they all confirm the view that the fluoro- has less interfering effect than the methoxy-group.[81] E. C. Kleiderer and R. Adams were unable to resolve 2 : 2′ : 6 : 6′-tetrafluoro-3 : 3′-dichlorodiphenyl-5 : 5′-dicarboxylic acid (IV), so the four fluoro-atoms are not sufficiently large to prevent free rotation of the phenyl groups. From this the authors also conclude that the envelope 0·5 Å. thick, surrounding atoms, which was suggested by N. V. Sidgwick [82] to represent the forces causing repulsion between non-linked atoms, must be much thinner, since on the basis of the diameters used by Sidgwick the tetrafluoro-atoms should collide and the acid should be resolvable. Experimentally the acid was not resolvable and did not show mutarotation of the salts with optically active bases even at 0°.

(IV.)





(V.)

A study of the acid (V) has given results of great interest. Five acids were synthesised [83] in which R was a methoxy-, methyl, chloro-, bromo-, or nitro-group. Only one brucine salt was isolated in each case, as the second salt in the solution passed into the first during the process of isolation. The active acids were obtained from the salts, but they racemised readily in organic solvents at room temperature. Since the substituents in the ortho-positions are the same in all five examples, it might be expected that all five acids would racemise at the same rate. Actually this is not so, for the 5-nitro-acid was the most stable, the 5-bromo- and the 5-chloro-acid equal and next in stability, and the 5-methyl- and the 5-methoxy-acid were the least stable. There are various ways of accounting for these differences, but evidence on the precise cause is lacking.

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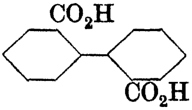
[80] R. W. Stoughton and R. Adams, *J. Amer. Chem. Soc.*, 1932, **54**, 4426; *A.*, 63.

[81] W. M. Stanley, E. McMahon, and R. Adams, *ibid.*, 1933, **55**, 706; *A.*, 392; E. C. Kleiderer and R. Adams, *ibid.*, p. 716; *A.*, 392; *ibid.*, p. 4219; A. M. Van Arendonk, M. E. Cupery, and R. Adams, *ibid.*, p. 4225; A. M. Van Arendonk, B. C. Becker, and R. Adams, *ibid.*, p. 4230.

[82] *Ann. Reports*, 1932, **29**, 70.

[83] H. C. Yuan and R. Adams, *J. Amer. Chem. Soc.*, 1932, **54**, 4434; *A.*, 63.

In 1930 W. M. Stanley and R. Adams [84] emphasised what F. Bell and P. H. Robinson [85] had said earlier, that many diphenyl derivatives had been studied with three or four *o*-groups but only one with two *o*-groups, namely, diphenic acid (VI), and this could not be resolved. On the basis of the former authors' mode of calculation it was found that the carboxyl group should fail to collide with the *o*-hydrogen atom of the opposing nucleus by 0·4 Å. Any groups which exceeded carboxyl by 0·4 Å. should lead to resolution and in this category were placed sulphonic acid groups, bromine, and iodine. Attempts to resolve diphenyl-2 : 2′-disulphonic acid (VII) by means of the diquinine, dibrucine, and dimorphine salts were unsuccessful, and so also were attempts to resolve 4 : 4′-diaminodiphenyl-2 : 2′-disulphonic acid.



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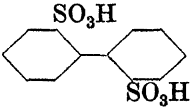

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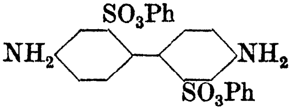

(VIII.)

The first demonstration of resolvability of this type was made by A. Corbellini and C. Pizzi [86] with 2-(hydroxydiphenylmethyl)-diphenyl-2′-carboxylic acid (IX; R = Ph), but for the most satisfying demonstration of the validity of Adams's deductions we are indebted to E. E. Turner and his colleagues. (Miss) M. S. Lesslie and Turner [87] were able to isolate both optically active modifications of phenyl benzidine-2 : 2′-disulphonate (VIII). This was soon followed by the successful resolution by the same authors [88] of diphenyl-2 : 2′-disulphonic acid (VII) by crystallisation of the strychnine hydrogen salt and of *o*-(2-dimethylaminophenyl)phenyltrimethylammonium iodide (X) by (Miss) F. R. Shaw and E. E. Turner[89] by means of camphor-10-sulphonic acid.

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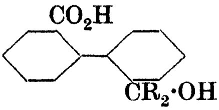
[84] *J. Amer. Chem. Soc.*, 1930, **52**, 4471; *A.*, **1931**, **79**.

[85] *J.*, 1927, 1696; *A.*, 1927, 876.

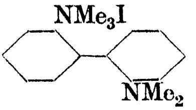
[86] *Atti R. Accad. Lincei*, 1932, [vi], **15**, 287; *A.*, 1932, 849.

[87] *J.*, 1932, 2021; *A.*, 1932, 942.

[88] *Ibid.*, p. 2394; *A.*, 1932, 1241.



(IX.)



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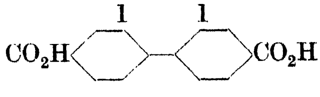
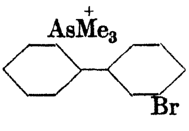


(XI.)

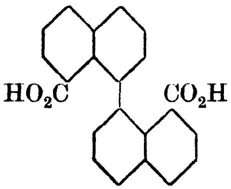
To these successful syntheses must be added another by N. E. Searle and R. Adams,[90] who crystallised 2 : 2′-di-iododiphenyl-4 : 4′-dicarboxylic acid (XI) with brucine and obtained the brucine salt of the *l*-acid only, since the *d*-acid changed in solution to the *l*-acid, which separated as the most sparingly soluble salt. In the meantime A. Corbellini and M. Angeletti[91] demonstrated the resolvability of another example of type (IX) in 2-α-hydroxy-α-methylethyldiphenyl-2′-carboxylic acid (IX; R = Me).

The successful outcome of these resolutions of diphenyl with only two ortho-substituents in opposite nuclei proves that the hydrogen atoms in the two remaining ortho-positions do act as obstacles and are not embedded in the nuclear carbon atoms. It naturally follows that a diphenyl with one ortho-substituent of sufficient size should be resolvable, provided that another substituent is present in the other nucleus, as was pointed out by F. R. Shaw and E. E. Turner.[89] Without this second substituent the substance would possess a plane of symmetry and be unresolvable. Evidence has been obtained by M. S. Lesslie and E. E. Turner[92] that the 2-(*m*-bromophenyl)-phenyltrimethylarsonium ion (XII) is capable of showing optical activity both in presence and in absence of an optically active anion.

A special class of diphenyl derivatives with only two out of the four ortho-positions occupied by substituents other than hydrogen is found in certain dinaphthyls. A. Corbellini[93] resolved 1 : 1′-dinaphthyl-8 : 8′-dicarboxylic acid (XIII) by means of its brucine,



(XII.)



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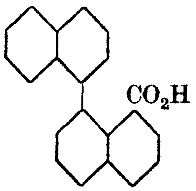

(XIV.)

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[89] *J.*, 1933, 135; *A.*, 388; *Nature*, 1932, **130**, 315; *A.*, 1932, 1125.

[90] *J. Amer. Chem. Soc.*, 1933, **55**, 1649; *A.*, 608.

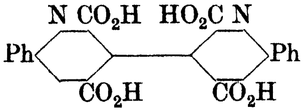
[91] *Atti R. Accad. Lincei*, 1932, [vi], **15**, 968; *A.*, 64.

[92] *Chem. and Ind.*, 1933, **52**, 19.

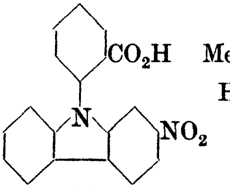
[93] *Atti R. Accad. Lincei*, 1931, [vi], **13**, 702; *A.*, 1932, 56.

cinchonine, and strychnine salts. The same acid was independently resolved by W. M. Stanley [94] by means of the quinine salt and by J. Meisenheimer and O. Beisswenger [95] by the brucine salt. The last-named observers also resolved the ethyl hydrogen salt of this acid with brucine, and the monocarboxylic acid (XIV) with brucine in ethyl acetate. A comparison of these dinaphthylcarboxylic acids with diphenic acid (VI) shows that carboxyl groups have a greater obstructing power in the former than in the latter, since they are attached to the ortho-positions of the diphenyl molecule through the rigid structure of the additional ring; they are in fact α-substituted acetic acid groups in the original diphenyl molecule supported rigidly in an obstructing position.

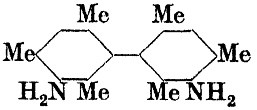
R. Adams and his co-workers have successfully extended the experimental study of restricted rotation to certain heterocyclic nitrogen compounds. The resolution of 1-*o*-carboxyphenyl-2 : 5-dimethylpyrrole-3-carboxylic acid and of 2 : 5 : 2′ : 5′-tetramethyl-1 : 1′-dipyrryl-3 : 3′-dicarboxylic acid was mentioned in an earlier *Report*.[96] A new type, a dipyridyl linked through carbon, 2 : 4 : 2′ : 4′-tetracarboxy-6 : 6′-diphenyl-3 : 3′-dipyridyl (XV), has now been resolved.[97] The optically active acids racemise readily in warm alcoholic solution, and the readiness with which this occurs is attributed to a diminution of the interfering effect of two carboxyls by the proximity of the nitrogen atoms. 9-*o*-Carboxyphenyl-2-nitrocarbazole (XVI) also has been resolved, the active forms racemising slowly at the ordinary temperature.[98]



(XV.)



(XVI.)



(XVII.)

The stability of the optically active forms in some cases is quite remarkable. Diaminodimesityl (XVII) was resolved and then submitted to 350 atmospheres pressure of hydrogen at 225° in the presence of active nickel. It was recovered unchanged in melting point and in molecular rotation.[99]

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[94] *J. Amer. Chem. Soc.*, 1931, **53**, 3104; *A.*, 1931, 1154.

[95] *Ber.*, 1932, **65**, [*B*], 32; *A.*, 1932, 270.

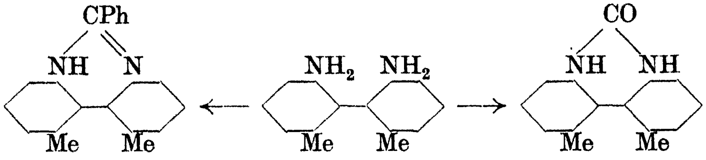
[96] *Ann. Reports*, 1931, **28**, 158.

[97] E. H. Woodruff and R. Adams, *J. Amer. Chem. Soc.*, 1932, **54**, 1977; *A.*, 1932, 755.

[98] W. I. Patterson and R. Adams, *ibid.*, 1933, **55**, 1069; *A.*, 513.

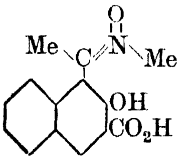
[99] C. R. Waldeland, W. Zartman, and H. Adkins, *ibid.*, p. 4234.

S. Sako [1] has been able to cyclise certain optically active diphenyls with retention of activity. *l*-3 : 3′-Diamino-2 : 2′-ditolyl (XVIII) is converted through its monobenzoyl derivative by phosphorus trichloride at 125° into *l*-2-phenyl-7 : 8-dimethyldiphenimidine (XIX), which can be re-hydrolysed to (XVIII). The *l*-diamine can be heated with urea at 210° to yield *l*-2-keto-7 : 8-dimethyl-2 : 3-dihydrophenimidine (XX). The preservation of optical activity in these cyclic derivatives shows that the diphenyl nuclei are probably co-axial but not co-planar.

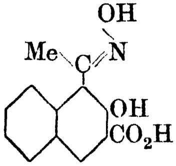


(XIX.) (XVIII.) (XX.)

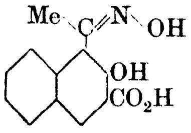
An ingenious use of the theory of restricted rotation has been made by J. Meisenheimer, W. Theilacker, and O. Beisswenger [2] for confirming the Hantzsch–Werner theory of the configuration of oximes. Ethyl 2-hydroxy-1-acetyl-3-naphthoate with methylhydroxylamine gives only one *N*-methyl ether of a ketoxime, which by hydrolysis at the ester group yields α-2-hydroxy-3-carboxy-1-naphthyl methyl ketoxime *N*-methyl ether (XXI). This acid was resolved by cinchonine, and from the salt the free acid was obtained with $[\alpha]_D + 124°$ as the sodium salt, which readily racemised at 70°. The resolution depends on the fact that free rotation of the group in the 1-position about the axis joining it to the naphthalene molecule is restricted by the adjacent hydroxyl group. The two simple oximes (XXII) and (XXIII) were both obtained and, although each formed well-crystallised alkaloidal salts, only those of the β-oxime acid (XXIII) indicated resolution. In the latter case cinchonine and coniine converted the whole of the racemic β-oxime acid into one optically active form. These salts racemise very readily and it was not possible to isolate the free optically active oxime even by working rapidly at —15°.



(XXI.)



(XXII.)



(XXIII.)

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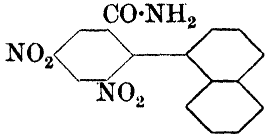
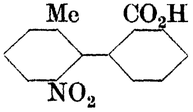
[1] *Mem. Coll. Eng. Kyushu*, 1932, **6**, 263; *A.*, 1932, 524.

[2] *Annalen*, 1932, **495**, 249; *A.*, 1932, 743.

Optically active diphenyls have also been made use of for investigating the mechanism of reactions. E. S. Wallis and W. W. Moyer[3] prepared *d*-3 : 5-dinitro-2-α-naphthylbenzamide (XXIV) by the method of M. S. Lesslie and E. E. Turner[4] and submitted it to the Hofmann change with sodium hypobromite. The corresponding *d*-amine was isolated of maximum rotation. F. Bell[5] has also announced the conversion of optically active 6-nitro-2-methyldiphenyl-2′-carboxylic acid (XXV) by the Hofmann and Curtius reactions into an amine of the same sign of rotation as the parent acid. In both cases the conclusion seems inevitable that the nuclear carbon atom " is already under the influence of the entering nitrogen atom before the ⁻C⁻C⁻ link is severed."



(XXIV.)



(XXV.)

Optical Activation.—The intensive study of the optically active diphenyls has brought into prominence the phenomenon of optical activation, a property of certain potentially active molecules which has on more than one occasion been hailed as new, novel, or anomalous but in reality goes back for more than thirty years for its first example. The substances represented by the formulæ (I), (V), and the half-ester of (XIII) in the preceding section, when crystallised with brucine, deposit the salt containing the *l*-acid as the most sparingly soluble component, and on further concentration of the mother-liquor only the same salt of the *l*-acid can be found. A facile interchange between the *d*- and *l*-forms takes place in the solvent and, the *l*-acid being removed from the solution by being sparingly soluble, leads to a regeneration of further quantities from the *d*-acid. The first record of this striking behaviour seems to be that described by W. J. Pope and S. J. Peachey,[6] who found that solutions of methylethyl-*n*-propyltin *d*-camphorsulphonate or α-bromocamphorsulphonate deposited only *d*-methylethylpropyltin salt on evaporation to dryness. A decade later, W. H. Mills and (Miss) A. M. Bain[7] showed that quinine and morphine salts of 4-oximino*cyclo*hexanecarboxylic acid, when evaporated, always gave one form of the optically active oxime and the authors considered the phenomenon to be one of activation rather than one of simple resolution. The same property was encountered by the same authors[8] with the morphine and quinine salts of the benzoylphenylhydrazone of *cyclo*hexanone-4-carboxylic acid. A striking example of the same phenomenon was recorded by H. Leuchs[9] in 1921, who found that, when hydrocarbostyril-3-carboxylic acid was crystallised from methyl alcohol with quinidine, the whole of the original racemic acid was obtained as the *d*-acid quinidine salt. Here the mechanism was quite clear, since the interchange between the *l*- and the *d*-form passed through a common enolic form, thus :

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[3] *J. Amer. Chem. Soc.*, 1933, **55**, 2598; *A.*, 821.

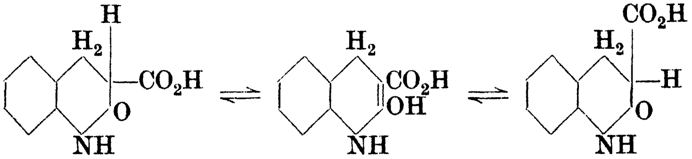
[4] *J.*, 1931, 1189; *A.*, 1931, 840.

[5] *Chem. and Ind.*, 1933, **52**, 584.

[6] *P.*, 1900, **16**, 12, 42, 116.

[7] *J.*, 1910, **97**, 1869.

l-acid salt ⇌ enolic acid salt ⇌ *d*-acid salt ⟶ crystals



The most instructive study of optical activation is to be found in a communication by J. Read and (Miss) A. M. McMath,[10] who showed that, when chlorobromomethanesulphonic acid is carefully crystallised with *l*-hydroxyhydrindamine, the whole of the racemic acid can be obtained as the *l*-acid *l*-base salt. So far the observations are but another example of what had already been described, but the authors made the further significant observation that in acetone solution there is a disturbed equilibrium between the diastereoisomerides in the proportion *l*B . *d*A (19%) ⇌ *l*B . *l*A (81%).

It would seem to follow from this that in the case of easily racemisable substances, when sufficient solvent is used for complete solution of the originally partially racemic salt, the position of equilibrium attained should not as a rule be that of the partially racemic salt but rather one where there is a greater or less preponderating amount of one of the diastereoisomerides over the other. Within recent years several examples of this disturbed equilibrium have been noted.

In 1927 R. Kuhn and O. Albrecht[11] showed that 4 : 4′-dinitrodiphenic acid (I) could be activated in alcoholic solution by quinine and by cinchonidine, but no salt could be isolated containing optically active acid. F. Bell and P. H. Robinson[12] also found evidence of activation of 4-nitrodiphenic acid (II) by quinine, and

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[8] *J.*, 1914, **105**, 66.

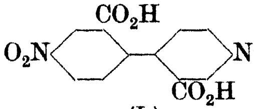
[9] *Ber.*, 1921, **54**, 830; *A.*, 1921, i, 442.

[10] *J.*, 1925, **127**, 1572; *A.*, 1925, i, 1126; *J.*, 1926, 2186; *A.*, 1926, 1024.

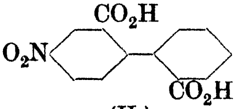
[11] *Annalen*, 1927, **455**, 272; *A.*, 1927, 876.

[12] *J.*, 1927, 2234; *A.*, 1927, 1069.

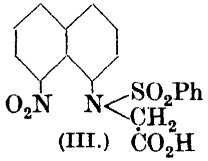
E. E. Turner and M. S. Lesslie[13] observed similar properties in quinine diphenate. Another example was found by W. H. Mills



(I.)



(II.)

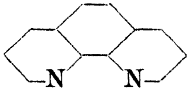


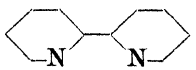
(III.)

and K. A. C. Elliott[14] in benzenesulphonyl-8-nitronaphthylglycine (III), which when combined with brucine in acetone solution gave straightway a brucine salt of one optically active form in 90% yield or over. Further, if equivalent quantities of brucine and inactive acid were dissolved separately in chloroform and the solutions mixed, the initial rotation due to the partial racemate fell with time to an equilibrium value due to partial activation of the acid.

In most of the above cases the solvents used have been organic solvents in which the degree of ionisation of the diastereoisomeric salts will not be large. The finding by P. Pfeiffer and his co-workers of examples of activation in aqueous solutions is therefore welcome. Pfeiffer and K. Quehl[15] found that when 3 equivalents of α-phenanthroline (IV) or 2 : 2′-dipyridyl (V) were added to an aqueous solution of zinc *d*-camphorsulphonate or *d*-α-bromo-π-camphorsulphonate the added base went into solution in combination with the zinc as a complex cation of the type $[\text{Zn phen}_3]^{++}$ and the rotation

(IV.)





(V.)

of the solution changed, becoming more lævorotatory in the case of camphorsulphonic acid and more dextrorotatory in the case of the bromo-acid. On the other hand ammonia, pyridine, and ethylenediamine were without action. There can be no doubt that octahedral ions of trisdipyridyl zinc and triphenanthroline zinc are formed and are activated by the optically active anions. Moreover the degree of activation can be increased by increasing the amount of camphorsulphonic acid.[16] Further, activation of zinc phenanthroline sulphate can be effected by addition of cinchonine hydrochloride, strychnine sulphate, or cinchonine methochloride, but not by cinchonine dimethochloride. Even nicotine base can produce some activation. In no case, however, could optically active zinc salts be isolated from the solutions. In a similar manner cadmium salts could be activated and in a later paper P. Pfeiffer and Y. Nakatsuka [17] extended the activation to nickel, cobalt, and manganese salts.

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[13] *Chem. and Ind.*, 1932, **51**, 493.

[14] *J.*, 1928, 1291; *A.*, 1928, 748.

[15] *Ber.*, 1931, **64**, [*B*], 2667; *A.*, 1932, 30.

[16] P. Pfeiffer and K. Quehl, *ibid.*, 1932, **65**, [*B*], 560; *A.*, 1932, 578.

As a classification of optical activations, R. Kuhn [18] has suggested that an activation which only occurs in the presence of optically active materials is an " asymmetric rearrangement of the first order," and an activation which persists on removal of the optically active inducer is an " asymmetric rearrangement of the second order." Such a classification is apt to suggest a discontinuity between the two phenomena, but experience in the diphenyl series, which is replete with examples, shows that the two phenomena merge one into the other.

In the ramifications of optical activity there are doubtless many observations which border on and link up with the phenomena here recorded, such, for example, as all the work on asymmetric synthesis, A. McKenzie and (Miss) I. A. Smith's observations on catalytic racemisation [19] where an optically active group acts asymmetrically in a desmotropic change, and G. Bredig and M. Minaeff's asymmetric synthesis with the aid of catalysts.[20]

Miscellaneous Resolutions.—Resolution by crystallisation in enantiomorphous forms was one of the methods originally introduced by Pasteur for the separation of enantiomorphs. The number of such resolutions on record is not large. During the past year Mme. Bruzau [21] has described the resolution of 4-methoxy-*ms*-methyldeoxybenzoin, $CHPhMe{\cdot}CO{\cdot}C_6H_4{\cdot}OMe$, by selection of the crystals by hand. Pasteur's second method of resolution, based on the difference in properties of the two diastereoisomerides formed when the substance to be resolved is combined with an optically active substance, is the method most commonly employed and the extremes of this method range from the fractional crystallisation of salts to the selective adsorption on a fibre such as wool. The use of addition compounds for resolutions is very uncommon. A. Windaus, F. Klänhardt, and R. Weinhold [22] resolved α-terpineol, *ac*-tetrahydro-β-naphthol, and carvomenthol by means of the additive compounds with digitonin, and R. Weiss and A. Abeles [23] formed an additive product of *sec.*-butylpicramide with *d*-β-naphthylcamphylamine and from the mother-liquor isolated a small quantity of *l-sec.*-butylpicramide, $[\alpha]_D$ − 2·6°. H. Sobotka and A. Goldberg[24] have used the remarkable additive properties of deoxycholic acid for definitely establishing slight resolution of methylethylacetic acid, phenylethylethanol, dipentene, and camphor.

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[17] *Ber.*, 1933, **66**, [*B*], 415; *A.*, 400.

[18] *Ibid.*, 1932, **65**, [*B*], 49; *A.*, 1932, 269.

[19] *J.*, 1924, **125**, 1587; *A.*, 1924, i, 1066.

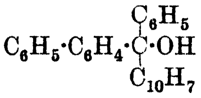
[20] *Biochem. Z.*, 1932, **249**, 241; *A.*, 1932, 967.

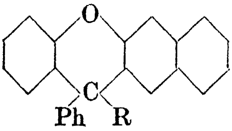
[21] *Compt. rend.*, 1933, **196**, 122; *A.*, 394.

[22] *Z. physiol. Chem.*, 1923, **126**, 308; *A.*, 1928, i, 586.

[23] *Monatsh.*, 1932, **59**, 238; *A.*, 1932, 398.

The possibility of using the optical properties of suitable dissymmetric triphenylmethane derivatives has often appealed to chemists and some measure of success has been attained during the past year. G. Karagunis[25] tried to prepare an optically active triarylmethyl chloride and from it the free radical, but was unsuccessful. This author with G. Drikos[26] has irradiated phenyl-*p*-tolyl-*p*-ethylphenylmethyl with circularly polarised light (4300 Å.) in presence of diluted gaseous chlorine at 0° and has observed a rotation of 0·1°. In the case of phenyldiphenylyl-α-naphthylmethyl a rotation of 0·2° is claimed. E. S. Wallis and F. H. Adams[27] have developed a general method of approach to the chemistry of optically active tercovalent carbon derivatives. The requisite carbinol, phenyldiphenylyl-α-naphthylcarbinol (I) or 12-phenyl-12-β-benzoxanthencarbinol (II; R = OH), was converted into its chloride (R = Cl), and the latter caused to react with thiolacetic acid. The thiolacetates formed could be readily resolved by brucine[28] or other alkaloids. *l*-12-Phenyl-12-β-benzoxanthenthiolacetic acid (II; R = $S{\cdot}CH_2{\cdot}CO_2H$), when treated with sodium in liquid ammonia and in absence of oxygen, yielded an orange-brown sodium triarylmethyl, which was decomposed by dry ammonium bromide. The resultant 12-phenyl-β-benzoxanthen had $[\alpha]_D$ − 11·7° in acetone. This indicated that the stability of a triarylmethyl anion with a complete octet of electrons (III) is at least temporary and also that the three co-valencies and the central carbon atom are not coplanar.

(I.)

$$C_6H_5{\cdot}C_6H_4{\cdot}\overset{C_6H_5}{\underset{C_{10}H_7}{C}}{\cdot}OH$$



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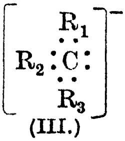
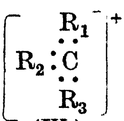
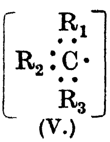


(III.)



(IV.)



(V.)

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[24] *Biochem. J.*, 1932, **26**, 905; *A.*, 1932, 930.

[25] *Dissert.*, Freiburg, 1926.

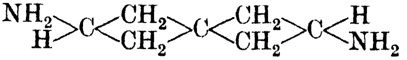
[26] *Naturwiss.*, 1933, **21**, 607; *A.*, 1041.

[27] *J. Amer. Chem. Soc.*, 1933, **55**, 3838; *A.*, 1167.

[28] E. S. Wallis, *ibid.*, 1932, **54**, 1695; *A.*, 1932, 611.

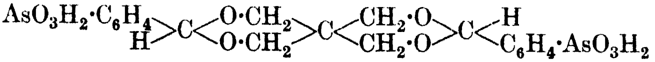
Attempts to prepare other optically active triarylmethyl derivatives from the active thiolacetates were invariably unsuccessful. This implies that the intermediate carbonium ion (IV) is optically unstable. Further, the optical instability of the free radical (V) was shown by the gradual loss of optical activity when *l*-phenyldiphenylyl-α-naphthylmethylthioacetic acid was allowed to react with triphenylmethyl in the presence of mercury. The rotation faded to zero after about 30 days.

The resolution of two compounds showing molecular dissymmetry is noteworthy. S. E. Janson and (Sir) W. J. Pope [29] have announced the resolution of diamino*spirocyclo*heptane (VI) by means of *d*- and *l*-camphor-β-sulphonic acids, the magnitude of the molecular rotatory power of the dihydrochlorides, $[M]_{4358} \pm 30°$, leaving no doubt as to the genuineness of the phenomenon. C. S. Gibson and B. Levin [30] have resolved *dl*-*spiro*bis-3 : 5-dioxan-4 : 4′-di(phenyl-*p*-arsonic acid) (VII) by means of *d*- and *l*-nor-ψ-ephedrines. The two enantiomorphous acids had $[\alpha]_{5461} \pm 24°$ in aqueous solution. The acetal nature of this substance is shown by the complete racemisation which occurs on conversion into the bis(dichloroarsine).



$$\substack{NH_2\\H}\!>\!C\!<\!\substack{CH_2\\CH_2}\!>\!C\!<\!\substack{CH_2\\CH_2}\!>\!C\!<\!\substack{H\\NH_2}$$

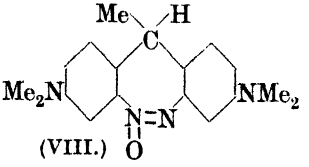
(VI.)



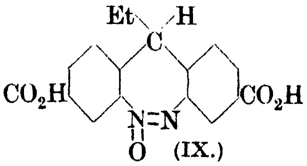
$$\substack{AsO_3H_2\cdot C_6H_4\\H}\!>\!C\!<\!\substack{O\cdot CH_2\\O\cdot CH_2}\!>\!C\!<\!\substack{CH_2\cdot O\\CH_2\cdot O}\!>\!C\!<\!\substack{H\\C_6H_4\cdot AsO_3H_2}$$

(VII.)

Finally, T. T. Chu and C. S. Marvel [31] have furnished an attractive and conclusive proof of the unsymmetrical nature of the azoxy-group by the use of optical properties. H. King [32] proposed to solve the problem by the resolution of methyl-2 : 2′-azoxy-4 : 4′-bisdimethylaminodiphenylmethane (VIII), and S. C. Hussey, C. S. Marvel, and F. D. Hagen [33] attempted to make ethyl-2 : 2′-azoxydiphenylmethane-4 : 4′-dicarboxylic acid (IX) but found that the product was polymeric.



(VIII.)



(IX.)

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[29] *Chem. and Ind.*, 1932, 316; *A.*, 1932, 508.

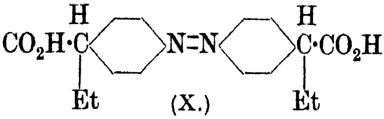
[30] *Proc. Roy. Soc.*, 1933, *A.*, **141**, 494; *A.*, 1177.

[31] *J. Amer. Chem. Soc.*, 1933, **55**, 2841; *A.*, 945.

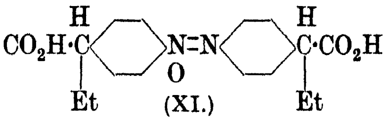
[32] *J. Soc. Chem. Ind.*, 1930, **49**, 281.

[33] *J. Amer. Chem. Soc.*, 1930, **52**, 1122; *A.*, 1930, 774.

Chu and Marvel have now prepared *meso*- and *dl*-α-*p*-azophenylbutyric acids (X) and have resolved the *dl*-compound. On oxidation of the *meso*- and the *dl*-compound with hydrogen peroxide, two azoxy-



(X.)



(XI.)

compounds (XI) were produced, both of which were resolved into optically active forms. If the azoxy-group had been symmetrical, the original *meso*-acid should have given an unresolvable *meso*-azoxy-compound.

Harold King.

ANALYTICAL CHEMISTRY.

THE continued application of physical methods to analytical problems is reflected in the large number of communications appearing during the period under review, depending mainly upon physical measurements. Opportunity is here taken to deal with one or two of these methods in some detail. Special attention has also been given to advances in gas analysis, since the methods now available furnish means for the more accurate and rapid analysis of gaseous mixtures. It is hoped that the short accounts given in this Report will achieve its object of placing before the reader the present position of a few chosen aspects of analytical chemistry; the references are full.

Polarographic Method.—Since we think that the "polarographic" method of Heyrovský and his co-workers should find wider application as a method of determining various cations, a short summary of the recent work in this field may be useful. The general theory of the method and its application were described some time ago.[1]

It need only be stated here that the expression upon which the method is based is in form similar to that for concentration cells, namely, $\pi_1 - \pi_2 = RT/nF \,.\ln C_1/C_2$, where π_1 is the so-called deposition potential of a molar solution referred to the normal calomel electrode, π_2 being the voltage of a more dilute solution of the same substance; π_1 is the point of inflexion of the current–voltage curve and is observed by a sudden upward surge in the curve, tables being available for its value for various cations. π_2 is the position of inflexion on dilution, and since the value $\pi_1 - \pi_2$ depends on the logarithm of the concentrations the displacement for a univalent cation on dilution from normal to decinormal is about 58 millivolts only at ordinary temperatures. For this reason, the point of inflexion does not move much on dilution, although the polarisation current makes a sudden jump at this point. If impurities are present, as for example traces of lead, zinc, or iron in common salt, these can be detected from the position of the onset of the "surge" in the curve, since each cation has its own deposition potential. The height of the surge as shown on the current–

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[1] See especially J. Heyrovský, *Rec. trav. chim.*, 1925, **46**, 488; *Bull. Soc. chim.*, 1927, **41**, 1224; *Z. anal. Chem.*, 1933, **91**, 206; *Mikrochem.*, 1933, **12**, 25.

voltage graph can be used to measure the quantity of the impurity provided the apparatus is calibrated for this purpose. The deposition potentials must be sufficiently separated to make a distinction possible, otherwise the method can only give the total quantity of the overlapping cations. In such cases various devices may be employed to distinguish the cations, such as rendering the solution alkaline, or forming complex ions with potassium cyanide. In general the method is very delicate, cations in concentration of about 10^{-6} g.-equiv. per litre being detectable.

Briefly, the apparatus used consists of a cathode formed by fine drops of mercury charged negatively, and a very large anode formed by a pool of mercury charged positively, upon which is placed the solution whose concentration is to be determined. A galvanometer of fair sensitivity is inserted in series with the cathode. The voltage on the anode is varied continuously by means of a rotating potentiometer from, say, 0 to 2 or 4. With the large mercury anode, a condition of non-polarisability is in practice secured. The movements of the galvanometer mirror are recorded, or photographed on a rotating drum for rapidity, and plotted against the voltage referred to the normal calomel electrode.

An application of the polarographic determination to alkali metals has been made[2] using tetramethylammonium hydroxide as the reference liquid, since the deposition potential of NMe_4 is $-$ 2·6 volts, that of lithium being $-$ 2·033 and of sodium and potassium very near $-$ 1·87 volts. It is not possible to determine the last two metals separately, but the estimation of the first in the presence of these alkalis is secured. Other metallic ions, provided they can be precipitated or converted into some complex, do not interfere with the determination of these alkalis. For example, calcium may be precipitated as phosphate, magnesium as hydroxide, and aluminium converted into an aluminate. If the separate proportions of sodium and potassium are desired, then the total alkali sulphate or chloride is determined gravimetrically and the usual calculation made. Consideration of the reactions occurring at the dropping mercury cathode shows that it is available for dealing with electro-reduction processes, and even the nitrate and nitrite anions may be estimated. It has been suggested[3] that the strong field in the neighbourhood of the cathode breaks up these ions in the first place into such powerfully charged atoms as N^{5+}, which presumably are then able to attract more anions towards the cathode surface, so replenishing the supply. This is assumed to occur as well as diffusion, without which no continuous measurements could be made. In neutral or alkaline solutions reduction takes place only if bi- or ter-valent cations are present in the liquid. For example, in a solution of $N/10$-lanthanum chloride the reduction potential is $-1{\cdot}2$ volts referred to the normal calomel electrode, and for nitrate eight faradays are required to give ammonia. Again, nitrite is decomposed by acids with the formation of nitric oxide, which is capable of easy electro-reduction, the increase of current in acid solutions occurring at $-0{\cdot}77$ volt. Very small concentrations of nitrate and nitrite can be determined;[4] for instance, it is claimed that quantities as small as 1 part of nitrous acid in 5×10^7 parts of an explosive may be estimated, and much less than this may be detected.

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[2] V. Majer, *Z. anal. Chem.*, 1933, **92**, 321; *A.*, 583.

[3] M. Tokuoka, *Coll. Czech. Chem. Comm.*, 1932, **4**, 444; *A.*, 1932, 1221.

An interesting application of the electro-reduction is the determination of nicotine[5] in the presence of pyridine and ammonium salts, as little as one part in ten million parts of tobacco being detectable. That the method is capable of more extended use is shown by the determination of cystine and cysteine in the hydrolysis products of proteins[6] from a comparison of the current–voltage curves with those of known quantities of the substances in solutions of cobalt chloride. Up to about 24 mg. per litre is stated to be the best concentration for accurate work.

Magneto-optical Method.—In the *Annual Reports* for 1930 a brief statement of the magneto-optical method for the detection of cations was given, and since then a number of papers has appeared dealing with the application of the method to the detection of isotopes, and in a few cases to the determination of cations. Without entering into discussion of the underlying principles of the " time lag " in the Faraday effect, it appears to be established that the procedure is capable of detecting, and in many cases estimating, certain cations even when these are present in extremely minute quantities. For example, calcium has been determined where large amounts of anions such as nitrate or phosphate and even when magnesium is present.[7] The method hitherto adopted was to alter the length of the circuit to the cell containing the solution under test, so that the " time lag " was counterbalanced. It is now found that by modifying the polarising system, it is possible to pass the current in the same direction through the cells containing the carbon disulphide and the solution under test, and by altering the setting of an analysing Nicol prism to determine the angle of rotation necessary to produce a minimum of light intensity.[8] The apparatus is calibrated by means of solutions of known concentrations of calcium chloride, allowance being made for the isotopes. The advantages claimed for this method of determining calcium are that it can be used for lower concentrations than any other method available, and that other substances do not interfere with the determination. Since the angle of rotation is stated to be the same for the same quantity of calcium in any of the compounds studied, it would appear that the method is available for calcium in any kind of material provided a clear solution of the calcium compound can be obtained. The process is somewhat limited in its application, not so much on the grounds of accuracy as from the fact that two observers are required, and that much practice is necessary to attain skill in working the apparatus, apart from the strain on the eyes of the observers. As the method is claimed to be available for the determination of as little as about 4×10^{-9} g. of calcium per litre, it will be seen that it has possibilities not possessed by any other analytical process hitherto proposed.

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[4] G. Semerano, *Giorn. Chim. ind. appl.*, 1932, **14**, 608; *A.*, 243.

[5] *Ibid.*, and *ibid.*, p. 1093.

[6] R. Brdička, *Coll. Czech. Chem. Comm.*, 1933, **5**, 238; *A.*, 964.

[7] E. R. Bishop and C. B. Dollins, *J. Amer. Chem. Soc.*, 1932, **54**, 4585; *A.*, 137.

Spectroscopic Methods.—The investigations reported are, in general, applications, extensions, or suggested improvements of the technique of modern practice. For quantitative work on emission spectra of the elements, usually metals, designed to estimate the proportion of a particular constituent, the methods commonly employed finally depend for their accuracy on two very general considerations: (1) determination of the intensity of spectrum lines as shown by equality of a photographic image of the lines from alloys or compounds of known composition, or comparison of the relative intensity of the lines visually or photographically, (2) evaluation of the intensity of the lines by use of the logarithmic wedge sector. In (1) difficulties arise from the necessity of obtaining uniformity in the production of arc or spark discharges if direct comparison on each occasion with a set of standard alloys is to be avoided. Methods for producing uniform conditions of excitation of arc and spark spectra are again discussed, and useful reviews of the conditions necessary for obtaining reproducible results are described in some detail.[9] In view of the difficulties of obtaining exactly reproducible discharges, it is desirable, if possible, to reproduce the luminosity of the spectral lines, for in this case the conditions of excitation of the spectrum are definite. One way of doing this is to arrange conditions of excitation in such a way that an arc line of an element of the alloy or metal under investigation is equal in intensity to that of a spark line of the same element, the two lines, arc and spark, being close together on the photographic plate. The electrical conditions of the circuit can then be varied in order to ascertain to what extent variations may be permitted without altering the apparent equality of intensity of the two lines. It is true that the preliminary search for such lines is tedious and the labour involved is great, but it is also apparent that the luminosity of the spectrum for any particular alloy is thereby fixed. This scheme has been employed with much success by Gerlach and his co-workers.[10] One of the best studies involving (2) is that of F. Twyman and F. Simeon,[11] the limitations of the method, and particularly the relation of intensity of illumination and blackening of the plates, being dealt with adequately. One essential condition for the application of the process is that the intensity of a spectrum line of one constituent of an alloy relative to that of a line of a second constituent should increase as the proportion of the first constituent increases, a condition which does not always necessarily follow with alloys. A variation of the more usual methods, which seems to be capable of extension beyond the cases given, namely, silicon in steel, chromium in nickel and barium–nickel alloys, has been described in some detail.[12] Arcs are used, and such a value of the arc current is chosen that a small change in current is accompanied by only a slight alteration in the relative intensity of the spectral lines. Furthermore, an intensity calibration pattern is photographed on the same plate as the spectrum, through a step diaphragm, thus providing a correct method for photographic photometry. This procedure renders unnecessary the considerations of the values of the plates and whether or not the lines under examination fall on straight portions of the characteristic curve of the plates. The relative densities of any two lines to be compared, *e.g.*, Ba 4554·0 and Ni 4546·9, are then determined by a microphotometer from a comparison with the density of the calibration pattern. Once a calibration curve for the range of a small constituent of an alloy is drawn, all similar alloys can be examined accurately by reference to the curve, for the ratio of the logarithms of the relative intensities of a pair of spectral lines is plotted against the proportion of the minor constituent. Here again it is to be noted that the curves of relative intensities can only be used for one type of alloy and that if another large constituent is added to the alloy a new curve is necessary. Better results can be obtained if the relative intensity of the pair of lines is referred to the proportion of the primary constituent of the alloy and not to the alloy as a whole. The logical method of calculation is atomic proportions of the constituents of the alloy.

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[8] E. R. Bishop, C. B. Dollins, and I. G. Otto, *J. Amer. Chem. Soc.*, 1933, **55**, 4365.

[9] O. Feussner, *Arch. Eisenhüttenw.*, 1932—1933, **6**, 551; F. Waibel, *Z. Metallk.*, 1933, **25**, 6; O. Feussner, *ibid.*, p. 73; *A.*, 800.

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[10] See W. Gerlach and E. Schweitzer, "Die Chemische Emissionsspektralanalyse."

[11] *Trans. Opt. Soc.*, 1930, **31**, 169.

[12] O. S. Duffendack, R. A. Wolfe, and R. W. Smith, *Ind. Eng. Chem.* (*Anal.*), 1933, **5**, 226; *A.*, 920.

An interesting application of the spectrographic method [13] is the quantitative study of the coprecipitation of cations with barium sulphate, a subject of great analytical interest for the accurate determination of sulphates. Carbon arcs were used and these were impregnated with solutions prepared from the precipitates, the quantity of coprecipitated cation being determined by comparison with prepared standards. Calcium and strontium are coprecipitated, but not beryllium, magnesium, or zinc, presumably in accordance with the rule that adsorption is likely to occur on polar crystals with ions which form slightly soluble compounds with the oppositely charged ions of the crystal lattice. The rule seems to break down for cadmium iodide, which is adsorbed on barium sulphate, and it is suggested that this is due to a preferential adsorption of the iodide ion and also of a CdI_4'' ion which is presumed to be formed from the slightly dissociating cadmium iodide in aqueous solutions.

For the more qualitative methods for the detection of various elements several investigations are recorded. An intermittent or flame arc is described [14] whereby such small amounts as 2×10^{-8} g. of arsenic or 10^{-7} g. of tellurium can be detected in solids. Beryllium may be detected in minerals after decomposition with hydrofluoric acid and conversion into chlorides, if the solution is excited by means of a high-frequency alternating arc of high potential.[15] The lines at 3131 and 2349 Å. are used, the first line detecting as little as 0·0001% in certain conditions. It has been found that certain elements exercise a marked damping on these emission lines, and that the damping increases in the order K, Na, Ba, Ca, Mg, Al, Si, an order following the ionisation potentials of these elements. A difficulty in the detection of some of the commoner elements in the minute quantities which can be found spectroscopically is the preparation of electrodes free from the elements sought for. If, for example, as little cadmium as 10^{-10} g. can be found, then the electrode of silver used must clearly be of special quality.[16]

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[13] L. Waldbauer and E. St. C. Gantz, *Ind Eng. Chem.* (*Anal.*), 1933, **5**, 311; *A.*, 1133.

[14] E. Riedl, *Z. anorg. Chem.*, 1932, **209**, 356; *A.*, 134.

[15] W. Kemula and J. Rygielski, *Przemysł Chem.*, 1933, **17**, 89; *A.*, 798.

[16] W. Späth, *Monatsh.*, 1932, **61**, 107; *A.*, 1932, 1220.

Fluorescence.—A useful device for work on fluorescence of solutions is designed to eliminate the troublesome spurious reddish-violet fluorescence sometimes seen when measurements of the true fluorescence colours are needed. This spurious fluorescence is the result of internal reflexions in the apparatus of the ultra-violet and far red regions of the exciting radiation. The interposition of a filter screen consisting of a solution of potassium nitrite is effective in suppressing the ultra-violet part of the spurious reflexions, permitting of more accurate examination of the scattered radiation.[17] The use of a screen of the nitrite is likewise effective in eliminating a large proportion of ultra-violet radiation when a mercury lamp is employed as the exciting source in studying the Raman effect.

X-Ray Spectrography.—Two important communications in *X*-ray spectrographic methods call for brief mention. The effect of the size of the particles and the necessity for employing very fine powders in quantitative *X*-ray chemical determinations has been discussed and investigated, and it is shown that the intensity of the diffracted ray may be decreased by irregularities in the surface of the target.[18] The molybdenum and the tungsten content of igneous rocks have been shown to be about $1{\cdot}5 \times 10^{-5}$ and $6{\cdot}9 \times 10^{-5}$ respectively. For determining the minute proportions here considered, the two elements are recovered from the mineral by precipitation with sodium hydroxide on a barium base, and the chlorides are volatilised from the precipitate by means of a stream of hot chlorine gas. The sublimed chlorides are then dissolved in acid, and molybdenum sulphide is coprecipitated with a substantial proportion of copper sulphide, the copper being subsequently removed by electrolysis. Molybdenum may then be determined colorimetrically. In the filtrate from the molybdenum sulphide, tungsten is estimated by the *X*-ray spectrograph.[19]

Staleness of Fish.—The range of application of electrometric methods is now so extensive that it is hardly surprising to find it applied to such a problem as estimating the relative freshness of haddock, and it will probably in due course be extended to other kinds of fish. At one end of the freshness scale the nose is doubtless an effective organ for the detection of loss of freshness, and at this stage further investigation is not informative. There are two changes in the decomposition of the proteins of fish which occur after rigor mortis begins to fade. In the first stage, due to enzyme action, autolysis begins and the proteins hydrolyse to polypeptides, peptones, and amino-acids. These substances are then broken

[17] E. Grünsteidl, *Mikrochem.*, 1933, **13**, 183; *A.*, 800.

[18] G. R. Fond, *J. Amer. Chem. Soc.*, 1933, **55**, 123, 127; *A.*, 242.

[19] G. von Hevesy and R. Hobbie *Z. anorg. Chem.*, 1933, **212**, 136; *A.*, 688.

down further by bacterial decomposition in the second stage to ammonia, amines, indole, skatole, hydrogen sulphide, and other substances. Many of these are basic, so that this decomposition is accompanied by a rise in p_H value. The second decomposition also occurs to some extent during autolysis, and the method employed is to titrate a solution prepared from the fish, first to p_H 6·0 and then to p_H 4·3—the range of p_H where the buffer effect of the inorganic phosphates is least. The amount of acid used in the first titration should be a measure of the degree of secondary bacterial decomposition, while the acid used in going from p_H 6 to p_H 4·3 should be in inverse proportion to the extent of the protein hydrolysis. The method of test is to use about 5 g. of finely minced flesh, shake it vigorously with about 100 ml. of water, and add excess of quinhydrone. With a platinum electrode and saturated calomel cell, titration is carried out using 0·0165*N*-hydrochloric acid. The amount of acid required to alter the original voltage of the fish extract to the voltage required for p_H 6·0 and then the amount for the step to p_H 4·3 are recorded, protein errors being disregarded. A discussion of the results and the significance of the variations in the quantity of acid used is described in detail.[20]

Ultimate Analysis.—The ter Meulen method of determining oxygen directly in organic substances has been found to give poor results on many occasions, and this has clearly been due to the employment of relatively inactive catalysts so that methane fails to be formed from the oxides of carbon, or to sublimation or too rapid volatilisation of the substance. A reinvestigation of the method [21] shows that satisfactory results can be obtained with all kinds of substance, ranging from oxalic acid to anthraquinone, provided active catalysts are used and suitable precautions taken. Asbestos-supported catalysts are undesirable, since the asbestos gives up water deposited on them very slowly, and the success of the determination depends mainly on the proportion of water formed. The catalysts recommended are platinum-coated quartz in fine granules or thoria-coated reduced nickel. Reported results for substances so far examined containing only carbon, hydrogen, and oxygen are good.

J. J. F.

Physical Properties of Solutions.—The simple oxygen-containing organic compounds are of considerable commercial importance and, as in many countries revenue interests are also involved, these substances have attracted and still attract much analytical attention.

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[20] M. E. Stansby and J. M. Lemon, *Ind. Eng. Chem.* (*Anal.*), 1933, **5**, 208.

[21] W. W. Russell and J. W. Fulton, *ibid.*, p. 384.

In the course of analysis, the compounds are usually obtained in the form of aqueous solutions. The simplest way of dealing with these is by physical methods, *e.g.*, determination of specific gravity, refractivity, etc., and for solutions of single substances, one of these will suffice. It frequently happens, however, that absolute knowledge of individual character is unknown, and in such cases it is necessary to obtain proof by agreement or non-agreement between two or more physical properties, possibly coupled with chemical evidence. To give a simple example, the refractivity of a dilute alcoholic distillate may agree with the ethyl alcohol strength as indicated by specific gravity; this may, however, be mere coincidence unless the absence of methyl alcohol is assured, since this low-refracting substance may otherwise be associated with a compensating quantity of a compound of higher refractive power.

The physical properties of mixed aqueous solutions are not strictly additive in character; nevertheless, if concentration is not too great, *e.g.*, up to 10%, such properties as specific gravity and refractivity of the substances under consideration are sufficiently additive that allowance can be made for the presence of compounds determined by other methods.

In the following account, which is intended to cover mainly the developments during recent years, occasional reference is made to earlier investigations.

Alcohols.—Of the lower aliphatic alcohols, methyl, ethyl and *iso*propyl are of first practical importance, *n*-propyl being relatively insignificant. Several sets of derivatives have been prepared, *e.g.*, phenylcarbamates (m. p.'s 47°, 51°, 90°, and 57° respectively) and *p*-xenylcarbamates (m. p.'s 127°, 119°, 138°, and 129°),[22] *p*-iodoxenylenecarbamates (m. p.'s 191°, 200°, —, and 189°),[23] *p*-nitrophenylcarbamates (m. p.'s 179°, 129°, 116°, and 115°),[24] 3 : 5-dinitrobenzoates (m. p.'s 107°, 92°, 122°, and 73°),[25] and α-naphthylcarbamates (m. p.'s 124°, 79°, 78°, and 105°). The *p*-nitrobenzoates can be isolated from dilute solutions of the alcohols.[26]

Methyl alcohol. There exist many very delicate tests for formaldehyde, and the majority of tests for methyl alcohol depend upon its preliminary oxidation to this compound; those in which the process is carried further to formic acid or carbon dioxide are generally less satisfactory.[27] Since the acetaldehyde produced on oxidation of ethyl alcohol interferes with many of these tests, the early applications of such methods to mixed alcohols were of little value. The process proposed by G. Denigès [28] was designed to meet the conditions imposed by these circumstances, and the method was later applied quantitatively.[29] Recent workers have found it advantageous to replace the sulphuric acid originally employed by phosphoric acid.[30] Some of these also give lists of substances which have been found to interfere and of those which do not; to the former class must be added dimethyl ether.[31] Many of the interfering substances, *e.g.*, glycerol and pectin, are readily separated by distillation.

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[22] G. T. Morgan and A. E. J. Pettet, *J.*, 1931, 1125.

[23] S. Kawai and K. Tamura, *Sci. Papers Inst. Phys. Chem. Res. Tokyo*, 1930, **13**, 270; *A.*, 1930, 1159.

[24] R. L. Shriner and R. F. B. Cox, *J. Amer. Chem. Soc.*, 1931, **53**, 1601; *A.*, 1931, 709.

[25] G. B. Malone and E. E. Reid, *ibid.*, 1929, **51**, 3424; *A.*, 1930, 58.

[26] H. Henstock, *J.*, 1933, 216.

Mixtures of methyl and ethyl alcohol may be evaluated rapidly by dilution with water to a total alcohol concentration of not more than 40%, which can then be ascertained from the specific gravity, since equal concentrations (by weight) of the two alcohols in water have practically the same density; the refractivity of the mixtures then serves to give the individual amounts of the alcohols.[32] If acetone and its homologues also be present, they may be removed by refluxing with paraformaldehyde in the presence of alkali, the excess of aldehyde being removed by oxidation with Fehling's solution prior to distillation.[33]

The use of 5 : 5-dimethyldihydroresorcinol (methone, dimedon) for fixing and characterising aldehydes, though not new,[34] has attracted considerable attention in recent years: [35] the formation of methylenedimethone has been utilised for the detection of very small quantities of methyl alcohol in ethyl alcohol.[36] The mixed aldehydes obtained by oxidation as in the Denigès process are distilled into ammonium chloride solution; evaporation now expels the acetaldehyde, and the formaldehyde, regenerated from the hexamethylenetetramine, is converted into its compound with methone. Photomicrographs of the distinctive precipitates from formaldehyde and acetaldehyde are on record.[37]

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[27] F. R. Georgia and R. Morales, *Ind. Eng. Chem.*, 1926, **18**, 304; *B.*, 1926, 381.

[28] *Compt. rend.*, 1910, **150**, 832; *A.*, 1910, ii, 461.

[29] C. Simmonds, *Analyst*, 1912, **37**, 16; *A.*, 1912, ii, 208; G. C. Jones, *ibid.*, 1915, **40**, 218; *A.*, 1915, ii, 493.

[30] F. R. Georgia and R. Morales, *loc. cit.*, ref. (27); R. M. Chapin, *J. Ind. Eng. Chem.*, 1921, **13**, 543; *A.*, 1921, ii, 598; L. O. Wright, *ibid.*, 1927, **19**, 750; *A.*, 1927, 687; H. Patzsch, *Pharm. Ztg.*, 1932, **77**, 1191; *B.*, 43; Berg, *ibid.*, p. 1262; *B.*, 91; H. Jeglinski, *ibid.*, 1933, **78**, 77; *B.*, 181.

[31] B. F. Dodge, *Ind. Eng. Chem.* (*Anal.*), 1932, **4**, 23; *A.*, 1932, 250.

[32] F. S. Mortimer, *Ind. Eng. Chem.*, 1927, **19**, 635; *A.*, 1927, 687; R. H. Field, M. W. Fairn, and J. M. Macoun, *J. Soc. Chem. Ind.*, 1931, **50**, 283T; *B.*, 1931, 963; J. M. Macoun, *ibid.*, p. 281T; *B.*, 1931, 963.

[33] R. W. Hoff and J. M. Macoun, *Analyst*, 1933, **58**, 749.

[34] D. Vorlander, *Ber.*, 1897, **30**, 1801; *A.*, 1897, i, 513; C. Neuberg and (Frl.) E. Reinfurth, *Biochem. Z.*, 1920, **106**, 281; *A.*, 1920, i, 914; W. Stepp, *ibid.*, 1922, **127**, 13; **130**, 578; *A.*, 1922, ii, 403, 793.

[35] D. Vorlander, *Z. anal. Chem.*, 1929, **77**, 241, 321; *A.*, 1929, 924, 949; G. Klein and H. Linser, *Mikrochem.*, 1929, Pregl Fest., 204; *A.*, 1929, 1292; L. Kofler and H. Hilbck, *ibid.*, **8**, 117; *A.*, 1930, 940.

[36] O. Mohr, *ibid.*, p. 154; *B.*, 1930, 651.

Ethyl alcohol. This, the most important of the compounds under consideration, is most frequently determined by physical methods, *e.g.*, specific gravity and refractivity. For this purpose, other substances must be eliminated, and for many of such of these as are not removed by distillation, the petroleum spirit separation was devised by T. E. Thorpe and J. Holmes.[38] Amongst compounds which are, at most, only partially removed by this method are methyl alcohol, *iso*propyl alcohol, and acetone; these are considered in other sections.

Of chemical methods, the process most used is that depending upon oxidation with chromic acid; among the applications of this process may be mentioned the determination of alcohol in urine, particularly in relation to the amount of alcoholic beverage consumed,[39] in alcoholic liquors,[40] and in breath.[41] S. G. Liversedge[42] holds that the results, for small amounts of alcohol, are comparable with those derived from specific gravity, upon which they provide a useful check.

A somewhat different oxidation process is the quantitative application of the reagent (dichromate in nitric acid) devised by H. Agulhon[43] for the detection of small quantities of alcohol and aldehyde in acetone; a positive reaction is given by primary and secondary alcohols, negative by tertiary alcohols.[44] The colour changes of the reagent itself are used to indicate the progress of the reaction, whose most important application is to the determination of ethyl alcohol in acetone.[45]

iso*Propyl alcohol.* A rapid method of determining the proportion of *iso*propyl alcohol in ethyl alcohol depends upon the varying solubility of sodium hydroxide in the mixture; the water content should be adjusted to not greater than 10%.[46] An apparatus and procedure have been devised for the isolation of pure anhydrous alcohol from extremely dilute solutions.[47]

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[37] H. Leffmann and C. C. Pines, *Bull. Wagner Free Inst.*, 1929, **4**, 15; *A.*, 1929, 1042.

[38] *J.*, 1903, **83**, 314.

[39] J. Evans and A. O. Jones, *Analyst*, 1929, **54**, 134; *A.*, 1929, 601.

[40] L. Semichon and M. Flanzy, *Ann. Falsif.*, 1929, **22**, 139; *B.*, 1929, 449; *ibid.*, p. 414; *A.*, 1929, 1266; *ibid.*, 1930, **23**, 347; *B.*, 1930, 1001; E. Kostuk, *Bull. Assoc. Chem. Sucr.*, 1930, **47**, 231; *B.*, 1930, 1087.

[41] L. Smith, *Svensk Kem. Tidskr.*, 1931, **43**, 83; *A.*, 1931, 990.

[42] *Analyst*, 1931, **56**, 595; *A.*, 1931, 1267.

[43] *Ann. Chim. analyt.*, 1912, **17**, 50; *B.*, 1912, 255.

[44] Cf. W. R. Fearon and D. M. Mitchell, *Analyst*, 1932, **57**, 372; *A.*, 1932, 718.

[45] E. C. Craven, *J. Soc. Chem. Ind.*, 1933, **52**, 239T; *B.*, 696.

*iso*Propyl alcohol is gradually extending its scope as a substitute for ethyl alcohol, not only in analytical operations,[48] but in numerous commercial preparations. Apart from a few direct colour reactions, such as those with piperonal [49] or *m*-nitrobenzaldehyde [50] and sulphuric acid, the majority of methods for detecting as well as for determining this alcohol depend on a preliminary chromic acid oxidation, tests being completed on the acetone formed thereby. Qualitatively, this compound may then be detected by means of nitroprusside [51] or by condensation with *o*-nitrobenzaldehyde to indigotin,[52] though it has been pointed out that certain other compounds containing the group –COMe also respond to the latter.[53] This test, due to Penzoldt,[54] has been applied quantitatively in the analysis of mixtures of acetone, ethyl alcohol, and *iso*propyl alcohol; [55] conditions are given for the chromic oxidation of the alcohols to acetic acid and acetone, respectively, which may be determined in the distillate. Another method of determining acetone is that involving the use of hydroxylamine hydrochloride [56] which is quite satisfactory in the presence of *iso*propyl alcohol.[57] On the whole, either of the above methods is preferable to Messinger's process in the presence of methyl, ethyl, or *iso*propyl alcohols, since these consume a certain amount of iodine.[58] Optimum conditions for the detection of acetone, acetaldehyde, ethyl alcohol, and lactic acid by the iodoform test have been prescribed.[59]

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[46] F. M. Archibald and C. M. Beamer, *Ind. Eng. Chem.* (*Anal.*), 1932, **4,** 18; *B.*, 1932, 250.

[47] A. O. Gettler, J. B. Niederl, and A. A. Benedetti-Pichler, *J. Amer. Chem. Soc.*, 1932, **54,** 1476; *A.*, 1932, 958.

[48] Cf. H. A. Schuette and M. P. Smith, *Ind. Eng. Chem.*, 1926, **18,** 1242; *B.*, 1927, 117; H. A. Schuette and L. E. Harris, *J. Amer. Pharm. Assoc.*, 1926, **15,** 166; *B.*, 1927, 118.

[49] G. Reif, *Z. Unters. Lebensm.*, 1928, **55,** 204; *B.*, 1928, 686; J. Wührer, *Pharm. Ztg.*, 1930, **75,** 845; *B.*, 1930, 980.

[50] T. Boehm and K. Bodendorf, *Arch. Pharm.*, 1930, **268,** 249; *B.*, 1930, 531.

[51] D. Henville, *Analyst*, 1928, **53,** 416; *B.*, 1928, 726; O. Noetzel, *Z. Unters. Lebensm.*, 1927, **53,** 388; *B.*, 1927, 668.

[52] R. Raw, *J. Soc. Chem. Ind.*, 1932, **51,** 276T; *A.*, 1932, 1235.

[53] R. J. W. Le Fèvre and J. Pearson, *ibid.*, 433T; *A.*, 377.

[54] *Deut. Arch. klin. Med.*, **34,** 127.

[55] C. A. Adams and J. R. Nicholls, *Analyst*, 1929, **54,** 2; *B.*, 1929, 162.

[56] Cf. O. Noetzel, *loc. cit.*, ref. (51); M. Krajčinovic, *Arhiv Hemiju*, 1932, **6,** 161; *B.*, 11.

[57] W. H. Simmons, *Perf. & Essent. Oil Rec.*, 1927, **18,** 168; *B.*, 1927, 504.

[58] L. F. Goodwin, *J. Amer. Chem. Soc.*, 1920, **42,** 39; *B.*, 1920, 280; H. A. Cassar, *Ind. Eng. Chem.*, 1927, **19,** 1061; *A.*, 1927, 1100.

Miscellaneous.—Individually, many of the chlorinated aliphatic hydrocarbons, *e.g.*, chloroform,[60] can be determined in terms of the chloride formed by saponification. This method cannot be applied to mixtures of chloroform with certain other members of the group; to such, the colorimetric test of S. Lustgarten [61] with β-naphthol can be applied quantitatively.[62] Amongst some microchemical tests for saccharin may be noted in particular that with copper and pyridine; [63] this reagent has also been applied to caffeine, theobromine, and theophylline [64] and to compounds of the veronal family; [65] for the last group, the formation of the complex substances has been adapted quantitatively in toxicological work.[66]

Reference was made at some length in last year's Report to the applications of organic compounds to inorganic analysis; this important class of reagent continues to attract attention, including in particular 8-hydroxyquinoline. This compound serves as a precipitant for tungstate [67] from acetic solution; in the presence of stannic salts, the precipitation should be effected in the presence of ammonium oxalate.[68] The presence of oxalate is also recommended in the precipitation of niobium.[69] Among the other rarer metals which have been investigated are gallium [70] and indium.[71] The utility of the reagent in recovering aluminium after removal of, or in the presence of, other metals or of phosphate has again been demonstrated.[72] The effect of p_H on the precipitation of magnesium, zinc, cobalt, nickel, copper, and molybdenum from acetate solutions has been carefully examined, and certain separations have been based on the findings under the specified conditions.[73] Calcium oxalate does not interfere with the bromometric titration of the magnesium compound; [74] the freshly ignited mixture of oxides obtained on ignition of the mixed precipitates yields its lime to 30% saccharate solutions.[75]

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[59] I. M. Korenman, *Z. anal. Chem.*, 1933, **93**, 335; *B.*, 821.

[60] G. D. Beal and C. R. Szalkowski, *J. Amer. Pharm. Assoc.*, 1933, **22**, 540; *B.*, 764.

[61] *Monatsh.*, 1882, **3**, 715; *A.*, 1883, 243.

[62] W. G. Moffitt, *Analyst*, 1933, **58**, 2.

[63] M. Wagenaar, *Mikrochem.*, 1932, **11**, 132; *Pharm. Weekblad*, 1932, **69**, 614; *A.*, 1932, 763, 867; J. J. L. Zwikker, *ibid.*, 1933, **70**, 551; *A.*, 732.

[64] L. Rosenthaler, *Pharm. Zentr.*, 1933, **74**, 288; *A.*, 732.

[65] J. J. L. Zwikker, *Pharm. Weekblad*, 1931, **68**, 975; *A.*, 1931, 1328.

[66] J. Peltzer, *Chem.-Ztg.*, 1933, **57**, 816.

[67] S. Halberstadt, *Z. anal. Chem.*, 1933, **92**, 86; *A.*, 366.

[68] A. Jílek and A. Ryšánek, *Coll. Czech. Chem. Comm.*, 1933, **5**, 136; *A.*, 584.

[69] P. Süe, *Compt. rend.*, 1933, **196**, 1022; *A.*, 585.

[70] L. Moser and A. Brukl, *Monatsh.*, 1929, **51**, 75; W. Geilmann and F. W. Wrigge, *Z. anorg. Chem.*, 1932, **209**, 129; *A.*, 43.

[71] Geilmann and Wrigge, *loc. cit.*

[72] J. Haslam, *Analyst*, 1933, **58**, 270; *A.*, 688; R. Lang and J. Reifer, *Z. anal. Chem.*, 1933, **93**, 161; *A.*, 799; G. Balanescu and (Mlle.) M. D. Motzoc, *ibid.*, 1932, **91**, 188; *A.*, 138.

7-Iodo-8-hydroxyquinoline-5-sulphonic acid has been used as a reagent for the colorimetric determination of ferric iron.[76] Other substituted derivatives have been found of value qualitatively; for instance, the 5:7-dibromo-compound reacts specifically for vanadium in fairly concentrated nitric acid solution, provided ferric iron has been removed,[77] whilst certain azo-derivatives are of value in detecting bivalent mercury [78] and magnesium.[79] The crystalline compound given by hydroxyquinoline–iodide reagent serves to detect bismuth at a dilution of one part in a million.[80]

Precipitation of $(\mathrm{Cu\,en_2})(\mathrm{HgI_4})$ in the presence of tartrate permits separation of mercury from numerous other heavy metals.[81] The complexes $(\mathrm{Cu\,pn_2})(\mathrm{AgI_2})_2$ and $(\mathrm{BiI_4})[\mathrm{Co\,en(SCN)_2}]$ serve in the rapid macro- and micro-determination of silver and bismuth respectively.[82]

In the separation and determination of copper and nickel by means of salicylaldoxime, for which details of procedure are given,[83] it is not necessary to isolate the reagent.[84]

Addition of 1-nitro-2-naphthol to a hot solution containing dilute sulphuric acid precipitates cobalt salts but not those of nickel or iron.[85] Accurate results in the determination of cobalt by means of dinitrosoresorcinol [86] are stated to be fortuitous, the precipitate

[73] H. R. Fleck and A. M. Ward, *Analyst*, 1933, **58**, 388; *A.*, 922.

[74] J. C. Redmond, *Bur. Stand. J. Res.*, 1933, **10**, 823; *B.*, 749.

[75] A. C. Shead and R. K. Valla, *Ind. Eng. Chem.* (*Anal.*), 1932, **4**, 246; *A.*, 1932, 588.

[76] J. H. Yoe, *J. Amer. Chem. Soc.*, 1932, **54**, 4139; *A.*, 43.

[77] G. Gutzeit and R. Monnier, *Helv. Chim. Acta*, 1933, **16**, 239; *A.*, 479.

[78] *Idem, ibid.*, p. 233; *A.*, 479.

[79] G. Gutzeit, R. Monnier, and R. Bachoulkova-Brun, *Arch. Sci. phys. nat.*, 1933, [v], **15**, Suppl., 203; *A.*, 1133.

[80] R. Sazerac and J. Pouzergues, *Compt. rend. Soc. Biol.*, 1932, **109**, 79; *A.*, 139.

[81] G. Spacu and G. Suciu, *Z. anal. Chem.*, 1933, **92**, 247; *A.*, 478.

[82] G. Spacu and P. Spacu, *ibid.*, 1932, **90**, 182; *A.*, 42; 1933, **93**, 260; *A.*, 924.

[83] H. L. Riley, *J.*, 1933, 895.

[84] S. Astin and H. L. Riley, *ibid.*, p., 314.

[85] A. Herfeld and O. Gerngross, *Z. anal. Chem.*, 1933, **94**, 7; *A.*, 1025.

[86] W. R. Orndorff and M. L. Nichols, *J. Amer. Chem. Soc.*, 1923, **45**, 1439; *A.*, 1923, ii, 584.

readily adsorbing reagent and alkali.[87] A similar effect is recorded [88] in the precipitation of cadmium by hexamethylenetetramine allyl iodide; [89] the use of β-naphthaquinoline in the presence of iodide [90] and of phenyltrimethylammonium iodide has been successfully applied to the determination of cadmium in spelter and zinc ores.[91]

A detailed investigation of the behaviour of small amounts of nickel in rock analysis indicated the desirability of determining this metal separately and of making allowance for the amount retained in the R_2O_3 precipitate; for very small quantities, α-furildioxime may advantageously replace dimethylglyoxime.[92] On account of solubility, nickel dimethylglyoxime should be filtered cold and washed with cold water; [93] the optimal p_H for precipitation is 7·5—8·1.[94] Nickel dicyanodiamidine [95] can be titrated with standard acid.[96] Zinc, cadmium, cobalt, nickel, and copper salts are quantitatively precipitated from neutral aqueous solutions by sodium anthranilate.[97]

2 : 2′-Dipyridyl gives a red coloration with ferrous salts in slightly acid solution : [98] this reagent has now been applied quantitatively, total iron being determined after reduction by sulphite.[99] For the colorimetric determination of aluminium with aurintricarboxylic acid, a modified procedure applicable to 0·0001 mg. of the metal has been described.[1]

The insolubility of magnesium calcium hexamethylenetetramine ferrocyanide is utilised in the quantitative separation of traces of magnesium for subsequent colorimetric comparison.[2] Qualitatively, hexamethylenetetramine has been used to separate iron, aluminium, and chromium from metals of the ammonium sulphide group.[3]

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[87] O. Tomiček and K. Komárek, *Chem. Listy*, 1932, **26**, 515; *Z. anal. Chem.*, 1932, **91**, 90; *A.*, 1932, 1224.

[88] L. C. Hurd and R. W. Evans, *Ind. Eng. Chem.* (*Anal.*), 1933, **5**, 16; *A.*, 245.

[89] V. Evrard, *Natuurwetensch. Tijds.*, 1929, **11**, 191; *A.*, 1930, 182.

[90] R. Berg and O. Wurm, *Ber.*, 1927, **60**, 1664; *A.*, 1927, 847.

[91] A. Pass and A. M. Ward, *Analyst*, 1933, **58**, 667.

[92] H. F. Harwood and L. S. Theobald, *ibid.*, p. 673; cf. B. A. Soule, *J. Amer. Chem. Soc.*, 1925, **47**, 981; *A.*, 1925, ii, 603.

[93] P. Nuka, *Z. anal. Chem.*, 1932, **91**, 29; *A.*, 138.

[94] T. Nagai, *Compl. Abs. Jap. Chem. Lit.*, 1932, **6**, 409.

[95] Cf. H. Grossmann and B. Schück, *Chem.-Ztg.*, 1907, **31**, 335; *A.*, 1907, ii, 582.

[96] J. V. Dubský and E. Hauer, *Mikrochem.*, 1933, **12**, 321; *A.*, 365.

[97] H. Funk and M. Ditt, *Z. anal. Chem.*, 1933, **91**, 332; **93**, 241; *A.*, 244, 924.

[98] F. Feigl and H. Hamburg, *ibid.*, 1931, **86**, 7; *A.*, 1931, 1261.

[99] F. Feigl, P. Krumholtz, and H. Hamburg, *ibid.*, 1932, **90**, 199; *A.*, 43; H. Müller, *Mikrochem.*, 1933, **12**, 307; *B.*, 366.

[1] P. S. Roller, *J. Amer. Chem. Soc.*, 1933, **55**, 2437; *A.*, 799.

[2] L. Debucquet and L. Velluz, *Compt. rend.*, 1933, **196**, 2006; *A.*, 922.

Diphenylthiocarbazone (dithizone), which has been investigated as a reagent for the detection of heavy metals,[4] has now been applied to the microchemical determination of lead and of copper.[5] Chlorides may be titrated in dilute acid solution against mercuric nitrate with diphenyl-carbazide or -carbazone as indicator.[6]

A sensitive test for gold with α-naphthylamine is described.[7] Alcoholic solutions of 2 : 3-diaminophenazine hydrochloride give coloured precipitates with neutral solutions containing Group II cations; [8] the colorations produced by 1 : 2-diaminoanthraquinone-3-sulphonic acid with copper, cobalt, and nickel salts are due to adsorption compounds.[9] Antipyrine and potassium iodide may be used to differentiate between ter- and quinque-valent antimony.[10]

B. A. E.

Electrometric Methods in Analytical Chemistry.

Potentiometric Methods.—The fundamental basis of potentiometric, as of ordinary, titration is that in the vicinity of the end-point (or equivalence-point) there is a very rapid change in the concentration of the titrant or of the substance titrated. The potentiometric method depends on the fact that the potential acquired by a suitable indicator electrode depends on the concentration of the ions with respect to which the electrode is reversible. At the equivalence-point there is a sudden change of electrode potential, and the plot of the *E.M.F.* of the cell, consisting of the indicator electrode and a reference (*e.g.*, calomel) electrode, against the volume of titrant added—the potential–titration curve—shows a marked inflexion. In general, it is assumed that the slope of this curve, $\Delta E/\Delta v$, where ΔE is the change of potential resulting from the addition of a definite volume Δv of titrant, is a maximum exactly at the required end-point. This is, however, only strictly true in certain limited cases, *viz.*, in the neutralisation of a strong acid and strong base, and in the precipitation of a salt of symmetrical valency type.[1] When a weak acid is neutralised by a strong base, the p_H at the point for which $\Delta E/\Delta v$ is a maximum is less than at the equivalence-point by $0{\cdot}65\sqrt{K_w/cK_a}$, where c is the acid concentration and K_w and K_a are the ionisation constants of water and acid, respectively.[2] The accuracy with which the point of maximum $\Delta E/\Delta v$ can be identified depends on the magnitude of the inflexion in the potential–titration curve; the smaller are c and K_a the smaller is the value of $\Delta E/\Delta v$, and if cK_a is less than $27K_w$ no inflexion occurs in the curve.[3] In precipitation reactions the inflexion will be before or after the true equivalence-point according as the ratio of the titrant ion to that of the titrated is greater or less than unity.[4] The titration error is less, and the magnitude of the inflexion greater, the lower the solubility of the precipitated salt;[5] in some instances this is decreased by the addition of an organic liquid.[6] For oxidation–reduction titrations the equivalence-point and that of maximum $\Delta E/\Delta v$ can theoretically never coincide, but the deviation is less the larger the equilibrium constant of the reaction; the value of $\Delta E/\Delta v$ at the end-point increases with this constant and the concentration of the solution.[7]

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[3] L. Lehrman, E. A. Kabat, and H. Weisberg, *J. Amer. Chem. Soc.*, 1933, **55**, 3509; *A.*, 1133; cf. P. Rây, *Z. anal. Chem.*, 1931, **86**, 13; *A.*, 1931, 1261.

[4] H. Fischer, *Mikrochem.*, 1930, **8**, 319; *A.*, 1931, 328; *Angew. Chem.*, 1933, **46**, 442, 517; *A.*, 799; H. Wölbling and B. Steiger, *ibid.*, 279; *A.*, 798.

[5] H. Fischer and G. Leopoldi, *Wiss. Veröff. Siemens-Konz.*, 1933, **12**, No. 1, 44, 52; *A.*, 923.

[6] J. V. Dubský and J. Trtílek, *Mikrochem.*, 1933, **12**, 315; *A.*, 364.

[7] H. Holzer and W. Reif, *Z. anal. Chem.*, 1933, **92**, 12; *A.*, 366.

[8] T. Pavolini, *Ind. chim.*, 1933, **8**, 692; *A.*, 799.

[9] J. V. Dubský and V. Bencko, *Z. anal. Chem.*, 1933, **94**, 19; *A.*, 1025.

[10] P. Duquénois, *Compt. rend.*, 1933, **197**, 339; *A.*, 921.

It is evident that, unless results of the highest accuracy are required or very dilute solutions are being analysed,[8] if an acid is reasonably strong, a precipitate not too soluble, or an oxidation–reduction reaction fairly complete, the end-point of a titration may be found from the point of inflexion in the potential–titration curve, or better from the plot of $\Delta E/\Delta v$ against v,[9] provided Δv represents *equal* volumes of titrant added.[10] For precision work the equivalence-point may be determined by calculation from potentials measured in its vicinity,[11] or from the values determined accurately at three or four points in the course of the titration.[12] A graphical method for determining the end-point on the potential–titration curve, which involves plotting its evolute,[13] has been proposed, but it is doubtful if it has any advantages.[14] Other special methods for finding the point at which $\Delta E/\Delta v$ is a maximum are discussed later in this Report.

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[1] E. D. Eastman, *J. Amer. Chem. Soc.*, 1925, **47**, 332; *A.*, 1925, ii, 594; I. M. Kolthoff and N. H. Furman, "Potentiometric Titrations," 2nd Edtn., 1931, p. 19.

[2] P. S. Roller, *J. Amer. Chem. Soc.*, 1928, **50**, 1; 1932, **54**, 3485; *A.*, 1928, 262; 1932, 1101.

[3] *Idem, ibid.*; see also F. Auerbach and E. Smolczyk, *Z. physikal. Chem.*, 1924, **110**, 65; *A.*, 1925, ii, 118.

[4] F. L. Hahn, M. Frommer, and R. Schulze, *ibid.*, 1928, **133** 390; *A.*, 1928, 857; B. Cavanagh, *J.*, 1930, 1425; *A.*, 1930, 1142.

[5] E. Lange and E. Schwartz, *Z. physikal. Chem.*, 1927, **129**, 111; *A.*, 1927, 1029; S. Glasstone, "The Electrochemistry of Solutions," 1930, p. 347.

[6] J. A. Atanasiu, *Compt. rend.*, 1926, **182**, 519; *A.*, 1926, 376; *J. Chim. physique*, 1926, **23**, 501; K. Schwartz and C. Schlösser, *Mikrochem.*, 1933, **13**, 18; *A.*, 582.

[7] I. M. Kolthoff and N. H. Furman, *op. cit.*, p. 55; S. Glasstone, *op. cit.*, p. 348.

[8] Compare E. Lange and R. Berger, *Z. Elektrochem.*, 1930, **36**, 980; *A.*, 1931, 186.

[9] J. C. Hostetter and H. S. Roberts, *J. Amer. Chem. Soc.*, 1919, **41**, 1337; *A.*, 1919, ii, 480.

[10] F. L. Hahn and M. Frommer, *Z. physikal. Chem.*, 1927, **127**, 1; *A.*, 1927, 743.

Indicator and Reference Electrodes.—The indicator electrode depends on the nature of the titration: for neutralisation processes some form of hydrogen electrode is required. The uses and limitations of the hydrogen gas, oxygen, and quinhydrone electrodes are well known,[15] although there have been some recent studies of technique,[16] but the glass electrode is worth special mention. The potential of this electrode follows that of the hydrogen electrode very closely over the range of p_H 0—9 and approximately up to p_H 12;[17] in very acid or alkaline solutions deviations are observed,[18] influenced sometimes by the cations in the solution.[19]

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[11] F. L. Hahn and M. Frommer, *Z. physikal. Chem.*, 1927, **127**, 1; see also F. L. Hahn, M. Frommer, and R. Schulze, *loc. cit.*; F. L. Hahn, *ibid.*, 1930, **146**, 363; *A.*, 1930, 560; *Z. anal. Chem.*, 1932, **87**, 263; *A.*, 1932, 353; F. L. Hahn and R. Klockmann, *Z. physikal. Chem.*, 1930, **146**, 373; 1931, **157**, 203, 206, 209; *A.*, 1930, 560; 1932, 33, 33, 24.

[12] B. Cavanagh, *loc. cit.*, ref. (4); *idem*, *J.*, 1928, 843, 855; *A.*, 1928, 607; F. Fenwick, *Ind. Eng. Chem.* (*Anal.*), 1932, **4**, 144; *A.*, 1932, 241.

[13] F. L. Hahn and G. Weiler, *Z. anal. Chem.*, 1926, **69**, 417; *A.*, 1927, 124.

[14] I. M. Kolthoff, *Rec. trav. chim.*, 1928, **47**, 397; *A.*, 1928, 496.

[15] W. M. Clark, "The Determination of Hydrogen Ions," 1928; H. T. S. Britton, "Hydrogen Ions," 2nd Edtn., 1932; S. Glasstone, *op. cit.*

[16] A. Thiel and G. Schulz, *Z. Elektrochem.*, 1930, **36**, 408; *A.*, 1930, 1009; L. Fletcher and J. B. Westwood, *J. Soc. Chem. Ind.*, 1930, **49**, 201T; *A.*, 1930, 1009; R. J. Best, *J. Physical Chem.*, 1930, **34**, 1815; *A.*, 1930, 1124; J. L. R. Morgan, O. M. Lammert, and M. A. Campbell, *J. Amer. Chem. Soc.*, 1931, **53**, 454, 597; *A.*, 1931, 456; *idem*, *Trans. Amer. Electrochem. Soc.*, 1932, **61**, 199; *A.*, 1932, 471; J. L. R. Morgan and O. M. Lammert, *J. Amer. Chem. Soc.*, 1931, **53**, 2154; *A.*, 1931, 914; O. M. Lammert and J. L. R. Morgan, *ibid.*, 1932, **54**, 910; *A.*, 1932, 699; I. M. Kolthoff and T. Kameda, *ibid.*, 1931, **53**, 821; *A.*, 1931, 585; B. Groák, *Biochem. Z.*, 1932, **245**, 61; *A.*, 1932, 486; P. Jolibois and G. Fouretier, *Compt. rend.*, 1932, **194**, 1072; *A.*, 1932, 486; L. Pincussen and J. Görne, *Biochem. Z.*, 1932, **249**, 126; *A.*, 1932, 924; W. Kordatski and P. Wulff, *Z. anal. Chem.*, 1932, **89**, 241; *A.*, 1932, 1013; P. L. du Noüy, *Compt. rend.*, 1932, **195**, 1265; *A.*, 242; J. A. V. Butler and G. Armstrong, *Trans. Faraday Soc.*, 1933, **29**, 862; *A.*, 1022.

[17] W. S. Hughes, *J.*, 1928, 491; *A.*, 1928, 370; D. A. MacInnes and D. Belcher, *J. Amer. Chem. Soc.*, 1931, **53**, 3315; *A.*, 1931, 1264.

[18] M. Dole, *ibid.*, 1931, **53**, 4260; 1932, **54**, 3095; *A.*, 1932, 126, 1207; G. Buchböck, *Z. physikal. Chem.*, 1931, **156**, 232; *A.*, 1931, 1237.

[19] W. S. Hughes, *loc. cit.*; M. Dole, *loc. cit.*; F. Urban and A. Steiner, *J. Physical Chem.*, 1931, **35**, 3058; *A.*, 1931, 1264; S. I. Sokolov and H. A. Passinski, *Z. physikal. Chem.*, 1932, **160**, 366; *A.*, 1932, 915.

The glass electrode can be used where other forms of the hydrogen electrode fail,[20] but it does not function satisfactorily in ethyl alcohol, in acetic acid,[21] or in the presence of gelatin.[22] Low melting-point glass of high electrical conductivity [23] is generally used in the form of a thin bulb or film,[24] but the resistance may still be of the order of 10—100 megohms. A quadrant electrometer [25] or a ballistic galvanometer,[26] in conjunction with a potentiometer, or a similar galvanometer, standardised by means of solutions of known p_{H},[27] have been used to measure the *E.M.F.*'s of glass-electrode cells; the most convenient methods, however, involve thermionic valve circuits.[28] The high resistance of the glass electrode may alter the characteristics of the valve and also introduce an error owing to the fall of potential due to the flow of grid current. The introduction of " electrometer " valves with very high grid to filament resistance and low grid current [29] permits the use of glass electrodes with resistances of the order of 1000 megohms. In spite of its relative insensitivity, an accuracy of ±0·05 millivolt has been claimed with the electrometer triode valve; [30] this is probably greater than the accuracy with which the liquid junction in the cell can be reproduced. For automatic registration purposes or to permit the use of robust instruments, the electrometer valve may be followed by further amplifying valves.[31] Another procedure for overcoming the resistance errors, not requiring special valves, is to balance the circuit first with the glass-electrode cell in one direction and then reversed, so that the grid circuit resistance remains constant; the mean of the two potentiometer readings gives the correct *E.M.F.* of the cell.[32] Whatever circuit is used it is essential that the grid current should be very small (less than 10^{-10} amp.), otherwise the electrode will polarise and yield erroneous results. Some workers operate the thermionic valve at its " floating grid " potential; the grid current is then zero and the anode current independent of the resistance of the glass electrode.[33] In this state the valve is, however, very

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[20] D. A. MacInnes and M. Dole, *Ind. Eng. Chem.* (*Anal.*), 1929, **1,** 57; *A.*, 1929, 673; L. W. Elder, *Trans. Amer. Electrochem. Soc.*, 1930, **57,** 383; *A.*, 1930, 565; F. Hazel and C. H. Sorum, *J. Amer. Chem. Soc.*, 1931, **53,** 49; *A.*, 1931, 304; C. Morton, *Trans. Faraday Soc.*, 1932, **28,** 84; *A.*, 1932, 342; H. T. S. Britton and R. A. Robinson, *ibid.*, p. 531; *A.*, 1932, 709; H. T. S. Britton and E. N. Dodd, *J.*, 1932, 1940; *A.*, 1932, 814; H. T. S. Britton and (Miss) B. M. Wilson, *ibid.*, p. 2550; *A.*, 1932, 1207; G. F. Davidson, *J. Text. Inst.*, 1933, **24**T, 185; *B.*, 587; J. W. Ingham and J. Morrison, *J.*, 1933, 1200; *A.*, 1118; T. F. G. Hepburn, *J. Soc. Leather Trades Chem.*, 1933, **17,** 268; *A.*, 689.

[21] M. Dole, *J. Amer. Chem. Soc.*, 1932, **54,** 3095; *A.*, 1932, 1207.

[22] R. J. Hartman and I. F. Fleischer, *J. Physical Chem.*, 1932, **36,** 1136; *A.*, 1932, 700.

[23] W. S. Hughes, *loc. cit.*; L. W. Elder, *J. Amer. Chem. Soc.*, 1929, **51,** 3266; *A.*, 1930, 50; D. A. MacInnes and M. Dole, *ibid.*, 1930, **52,** 29; *A.*, 1930, 423.

[24] *Idem, locc. cit.*; G. B. Harrison, *J.*, 1930, 1528; *A.*, 1930, 1151; G. R. Robertson, *Ind. Eng. Chem.* (*Anal.*), 1931, **3,** 5; *A.*, 1931, 449; G. D. Greville and N. F. Maclagan, *Trans. Faraday Soc.*, 1931, **27,** 210; *A.*, 1931, 801; M. R. Thompson, *Bur. Stand. J. Res.*, 1932, **9,** 833; *A.*, 367; E. C. Gilbert and A. Cobb, *Ind. Eng. Chem.* (*Anal.*), 1933, **5,** 69; *A.*, 248; D. A. MacInnes and D. Belcher, *ibid.*, p. 199; *A.*, 689; J. W. Ingham and J. Morrison, *loc. cit.*

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[27] C. Morton, *J. Sci. Instr.*, 1930, **7,** 187; *A.*, 1930, 1009; this method is only satisfactory if the temperature of the glass electrode is carefully controlled (private communication from Dr. C. Morton).

[28] W. C. Stadie, *J. Biol. Chem.*, 1929, **83,** 477; *A.*, 1929, 1262; G. B. Harrison, *loc. cit.*; G. Schwarzenbach, *Helv. Chim. Acta*, 1930, **13,** 865; *A.*, 1930, 1526; R. J. Fosbinder, *J. Physical Chem.*, 1930, **34,** 1294; *A.*, 1930, 883; R. J. Fosbinder and J. Schoonover, *J. Biol. Chem.*, 1930, **88,** 605; *A.*, 1930, 1376; D. Dubois, *ibid.*, p. 729; *A.*, 1931, 58; F. Müller, *Z. Elektrochem.*, 1930, **36,** 923; *A.*, 1931, 43; *idem, Z. physikal. Chem.*, 1931, **155,** 451; *A.*, 1931, 1129; *idem, Z. angew. Chem.*, 1931, **44,** 698; *A.*, 1931, 1144; *idem, Trans. Amer. Electrochem. Soc.*, 1932, **62,** 117; *A.*, 1932, 999; F. Müller and

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[30] G. D. Greville and N. F. Maclagan, *loc. cit.*; A. S. McFarlane, *loc. cit.*

[31] C. Morton, *J.*, 1931, 2977; 1932, 2469; *A.*, 1932, 24, 1105; J. J. Fox and L. G. Groves, *J. Soc. Chem. Ind.*, 1932, **51**, 7T; *B.*, 1932, 323.

[32] G. Schwarzenbach, *loc. cit.*; C. Morton, *J.*, 1931, 2983; *A.*, 1932, 24.

[33] R. J. Fosbinder; R. J. Fosbinder and J. Schoonover; D. Dubois, F Müller, W. C. Stadie, H. O'Brien, and E. P. Laug; H. M. Partridge and S. J. Broderick, *locc. cit.*

unstable, and slight positive deviations of the grid potential cause a large flow of grid current and serious polarisation may result.[34] Various devices have been used to eliminate galvanometer drift; [35] one of the simplest and most effective is to connect a ballistic galvanometer, acting as a null instrument, in series with a blocking condenser across a resistance in the anode circuit.[36] Accurate results with the glass electrode are obtained by using a pure sodium–calcium–silicate glass, by avoiding leakages over the surface of the glass and in the grid circuit,[37] and by providing adequate shielding.[38]

The Sb/Sb_2O_3 electrode, the antimony electrode, is attracting attention as a hydrogen-ion indicator; it is of the metal–metal oxide type [39] and so should behave theoretically as an oxygen electrode, its potential depending on the p_H of the solution. There is generally sufficient oxide on the surface of cast antimony not to require its addition to the solution,[40] but some workers prefer to add the oxide in a crystalline form.[41] Antimony deposited by the electrolysis of its trichloride in acetone is said to give very satisfactory electrodes.[42] In the range of p_H 2—7 antimony electrodes can behave reversibly, but in more alkaline solutions deviations occur; [43] they may still, however, be used for potentiometric titrations.[44] The antimony electrode is not readily poisoned [45] and is finding increasing application,[46] although it does not always

[34] C. Morton, *loc. cit.*

[35] G. Schwarzenbach; W. C. Stadie, H. O'Brien, and E. P. Laug; A. E. J. Vickers, J. A. Sugden, and R. A. Bell; F. Müller and G. Meyer, *locc. cit.*

[36] C. Morton, *J.*, 1931, 2977; *A.*, 1932, 24.

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[39] L. R. Parks and H. C. Beard, *J. Physical Chem.*, 1933, **37**, 821, 822; *A.*, 913.

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[45] M. Catenacci, *L'Ind. sacc. Ital.*, 1931, **24**, No. 8; *idem*, *Int. Sugar J.*, 1932, **34**, 185; *A.*, 1932, 586.

[46] F. Fenwick and E. Gilman, *J. Biol. Chem.*, 1929, **84**, 605; *A.*, 1930,

function satisfactorily.[47] A tungsten wire or rod also behaves as an oxygen electrode; its potential varies with the p_H of the electrolyte, but not in a reversible manner. It has been used for the potentiometric titration of a number of acids.[48] Other metals, and even non-metals, acquire more or less definite potentials, but they do not always adjust themselves rapidly to the changing p_H of the electrolyte.[49] This has been utilised in the " bimetallic " systems for simplified potentiometric titration wherein one metal, or a non-metal, acts as reference electrode and the other as indicator. During the titration the *E.M.F.* of the cell remains almost constant, but at the end-point one electrode, being more reversible than the other, responds more readily to the change of p_H so that there is a marked *E.M.F.* change. The following bimetallic systems have been found suitable for acid–base titrations : platinum and graphite, iron and antimony–cadmium alloy, antimony and antimony–lead alloy, bismuth and silver, antimony and copper amalgam, copper and cupric oxide, tungsten and silicon, copper, nickel, cobalt, or silver;[50] pure carborundum is said to make a very satisfactory reference electrode.[51] The polarised bimetallic system (*vide infra*) has also been used in neutralisation processes.[52]

For oxidation–reduction reactions smooth platinum is almost invariably the indicator electrode; the calomel reference electrode

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[48] J. R. Baylis, *Ind. Eng. Chem.*, 1923, **15**, 852; H. C. Parker, *ibid.*, 1925, **17**, 737; *A.*, 1925, ii, 899; H. T. S. Britton and E. N. Dodd, *J.*, 1931, 829; *A.*, 1931, 699.

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[51] B. Kamienski, *Z. physikal. Chem.*, 1928, **138**, 345; 1929, **145**, 48; *A.*, 1929, 144; 1930, 57.

[52] H. H. Willard and F. Fenwick, *J. Amer. Chem. Soc.*, 1923, **45**, 715; *A.*, 1923, ii, 286; A. H. Wright and F. H. Gibson, *Ind. Eng. Chem.*, 1927, **19**, 749; *A.*, 1927, 637.

may be used, but the development of bimetallic systems often makes this unnecessary. Although platinum rapidly acquires the oxidation–reduction potential of a solution, other metals, *e.g.*, palladium, gold, tungsten, and amalgamated gold, do not do so; the *E.M.F.* of a cell consisting of platinum and one of these metals consequently changes very rapidly in the vicinity of the end-point of an oxidation–reduction titration.[53] A further modification obviates the use of a potentiometer, the end-point being indicated by the maximum swing of a galvanometer in series with the cell and a high resistance.[54] For certain titrations it is even possible to use a cell consisting of two different platinum electrodes,[55] but more reliable results are obtained if two similar electrodes are polarised by a small current (*ca.* 5×10^{-6} amp.); the *E.M.F.* of the polarised cell, measured on a potentiometer, changes sharply as the equivalence-point is attained.[56] If one of the reactants or resultants of an oxidation–reduction process is an efficient depolariser and the other not, the simple " dead-stop " end-point method may be used.[57] A very small *E.M.F.* is applied to two platinum wires placed in the solution to be oxidised, *e.g.*, thiosulphate, so as just to balance the polarisation *E.M.F.* but to permit no current to flow; on the addition of the oxidant, *e.g.*, iodine, the current remains at zero until the end-point, when the first excess depolarises the cathode and so current flows and the galvanometer is deflected. In a recent modification the grid current from a thermionic valve, which is given a positive bias, polarises the electrodes; the change of *E.M.F.* at the end-point is indicated by a galvanometer in the anode circuit.[58]

When the titration involves a precipitation reaction the indicator electrode is generally of the metal forming the insoluble salt, *e.g.*, silver or mercury, although certain inert materials can replace silver in titrations with silver nitrate; [59] the reason for this is obscure.[60] Bimetallic systems, both unpolarised [61] and polarised,[62] have been used to follow the course of precipitation processes. The formation of complex ions can also be adapted to potentiometric titration, the indicator material being one of the elements present in the complex.[63]

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[54] N. H. Furman and E. B. Wilson, *J. Amer. Chem. Soc.*, 1928, **50**, 277; *A.*, 1928, 382.

[55] G. G. Reissaus, *Z. anal. Chem.*, 1926, **69**, 450; *A.*, 1927, 126; E. Müller and H. Kogert, *Z. physikal. Chem.*, 1928, **136**, 437; *A.*, 1928, 1203; *Z. anal. Chem.*, 1928, **75**, 235; *A.*, 1929, 42.

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[57] C. W. Foulk and A. T. Bawden, *ibid.*, 1926, **48**, 2045; *A.*, 1926, 927; (Miss) M. E. Pring and J. F. Spencer, *Analyst*, 1930, **55**, 375; *A.*, 1930, 1011; see also B. F. Brann and M. H. Clapp, *J. Amer. Chem. Soc.*, 1929, **51**, 39; *A.*, 1929, 286.

[58] J. L. Kassner, R. B. Kunze, and J. N. Chatfield, *ibid.*, 1932, **54**, 2278; *A.*, 1932, 814; K. Masaki and O. Hirabayashi, *Bull. Chem. Soc. Japan*, 1933, **8**, 245; *A.*, 1132.

Simplified Methods.—In addition to those mentioned for special cases, a number are applicable to all types of titration. If a reference electrode is used having the potential the indicator electrode will acquire at the end-point, the *E.M.F.* of the cell will be zero at this point, which may be detected by a reversal of current indicated on a galvanometer.[64] The reference solutions may be made from the actual reactants, or the required potential may be obtained in other ways; [65] the method is useful when many titrations of the same type have to be performed, one reference solution being adequate. Another method is to oppose the *E.M.F.* of the titration cell, consisting of indicator and reference (calomel) electrodes, by one equal to that the cell will have at the end-point.[66] A further modification, applicable to acid–base and silver–halide titrations, involves the construction of a simple cell, with quinhydrone and silver halide electrodes, which has zero *E.M.F.* at the required equivalence-point.[67]

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[59] E. Müller, *Z. Elektrochem.*, 1924, **30**, 420; *A.*, 1924, ii, 777.

[60] W. Böttger and B. M. Schall, *Z. physikal. Chem.*, 1933, **165**, 398; *A.*, 920.

[61] R. G. van Name and F. Fenwick, *J. Amer. Chem. Soc.*, 1925, **47**, 9; *A.*, 1925, ii, 594; J. A. Atanasiu and A. J. Velculesco, *Z. anal. Chem.*, 1931, **85**, 120; *A.*, 1931, 1260; W. Hiltner, *loc. cit.*

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[64] J. Pinkhof, *Chem. Weekblad*, 1919, **16**, 1163; *A.*, 1920, ii, 120 (see I. M. Kolthoff and N. H. Furman, *op. cit.*, p. 96); W. D. Treadwell, *Helv. Chim. Acta*, 1919, **2**, 672; *A.*, 1920, ii, 119; W. D. Treadwell and L. Weiss, *ibid.*, p. 680; *A.*, 1920, ii, 119; T. Callan and S. Horrobin, *J. Soc. Chem. Ind.*, 1928, **47**, 329T; *B.*, 1929, 154; B. L. Clarke and L. A. Wooten, *Ind. Eng. Chem.* (*Anal.*), 1931, **3**, 402; *B.*, 1931, 241.

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[67] B. Cavanagh, *J.*, 1927, 2207; *A.*, 1927, 1045; L. V. Wilcox, *Ind. Eng. Chem.* (*Anal.*), 1932, **4**, 38; *A.*, 1932, 242.

The *E.M.F.* of a cell consisting of two identical electrodes immersed in two solutions, representing the titration system before and after the addition of a definite volume of titrant respectively, is a direct measure of $\Delta E/\Delta v$, and should be a maximum at the end-point; this is the principle of "differential titration," the maximum being detected by the deflexion of a galvanometer.[68] In the first applications, two beakers and burettes were used;[69] in the later modifications the electrodes are placed in the same vessel, but by means of special devices a small quantity of the titrated solution surrounding one of the electrodes is temporarily kept from mixing with the bulk of the solution before each addition of titrant.[70] These methods are simple, do not require standard cell, reference electrode, or potentiometer, and are capable of considerable accuracy.[71] Thermionic-valve circuits for continuous reading of *E.M.F.* may be used for potentiometric titration,[72] and these permit of a special application of the differential method.[73] After each addition of titrant a compensating current is adjusted to bring the reading of the galvanometer in the anode circuit to zero; the deflexion resulting from the addition of a definite volume of titrant (0·05 c.c.) is then a direct measure of $\Delta E/\Delta v$.

The majority of reactions used in volumetric analysis, and many others for which suitable indicators are not available, can be studied potentiometrically; a large number of processes has already been listed,[74] and in addition titrations of the following elements, compounds, or mixtures may be noted: boric acid,[75] a strong acid in the presence of salts of weak acids,[76] nitrites,[77] lead,[78] ferrous ions,[79] osmium,[80] hypophosphoric acid,[81] ferrocyanide by mercuric, nickel, cobalt, ferric, and silver salts,[82] iron in felspar,[83] platinum and gold,[84] carbon dioxide,[85] hypochlorite and chlorate,[86] arsenite,[87] potassium,[88] cyanamides and cyanides,[89] very dilute solutions of silver, mercury, copper, chloride and iodide,[90] chromate and ferricyanide,[91] hydrazine with bromate and iodine,[92] tri- and tetra-thionates,[93] fluorides,[94] sulphate,[95] antimony,[96] silver chloride–thiosulphate mixtures,[97] chromic acid,[98] iron, vanadium, and nickel in steels,[99] zinc,[1] and free alkali in phenoxides.[2]

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[72] K. H. Goode, *J. Amer. Chem. Soc.*, 1922, **44**, 26; 1925, **47**, 2483; *A.*, 1922, ii, 307; 1925, ii, 1196; *J. Opt. Soc. Amer.*, 1928, **17**, 59; *A.*, 1928, 1109; D. F. Calhane and R. E. Cushing, *Ind. Eng. Chem.*, 1923, **15**, 1118; W. D. Treadwell and C. Paoloni, *Helv. Chim. Acta*, 1925, **8**, 89; *A.*, 1925, ii, 595; H. Bienfait, *Rec. trav. chim.*, 1926, **45**, 166; *A.*, 1926, 260; J. W. Williams and T. A. Whitenack, *J. Physical Chem.*, 1927, **31**, 519; *A.*, 1927, 434; C. G. Pope and F. W. Gowlett, *J. Soc. Instr.*, 1927, **4**, 380; *A.*, 1927, 1049; see also P. Jolibois and G. Fouretier, *Compt. rend.*, 1932, **194**, 872; *A.*, 1932, 486.

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[86] B. Troberg, *Z. anal. Chem.*, 1932, **91**, 161; *A.*, 135; A. Rius and V. Arnal, *Anal. Fis. Quim.*, 1933, **31**, 325; *A.*, 1022.

[87] I. C. Schoonover and N. H. Furman, *J. Amer. Chem. Soc.*, 1933, **55**, 3123; *A.*, 1023.

[88] B. P. Nicolski, and I. N. Lavrov, *Proc. Leningrad Dept. Inst. Fert.*, 1933, **17**, 45; *A.*, 922.

[89] H. Sinozaki, *J. Soc. Chem. Ind. Japan*, 1933, **36**, 145; *A.*, 798.

[90] R. Spychalski, *Rocz. Chem.*, 1933, **13**, 236; *A.*, 798; K. Schwarz, *Mikrochem.*, 1933, **13**, 6; *A.*, 581; K. Schwarz and C. Schlösser, *ibid.*, p. 18; *A.*, 582; K. Schwarz and T. Kantor, *ibid.*, p. 225; *A.*, 799; R. Flatt and A. Boname, *Bull. Soc. chim.*, 1932, [iv], **51**, 761; *A.*, 1932, 1009; R. Tronstad, *K. Norske Vidensk. Selsk. Forhandl.*, 1931, **4**, 20; *A.*, 42.

[91] C. del Fresno and E. Mairlot, *Z. anorg. Chem.*, 1933, **212**, 331; *A.*, 800; *idem*, *Anal. Fis. Quim.*, 1933, **31**, 122; *A.*, 924.

[92] O. Stelling, *Svensk Kem. Tidskr.*, 1933, **45**, 4; *A.*, 363.

[93] F. Ishikawa and T. Murooka, *Sci. Rep. Tôhoku Imp. Univ.*, 1932, **21**, 527; *A.*, 363.

[94] N. Allen and N. H. Furman, *J. Amer. Chem. Soc.*, 1933, **55**, 90; *A.*, 242.

[95] J. A. Atanasiu and A. J. Velculesco, *Z. anal. Chem.*, 1932, **90**, 337; *A.*, 363.

[96] W. Pugh, *J.*, 1933, 1; *A.*, 246.

Conductometric Titrations.—Many reactions involving the formation of a sparingly soluble or feebly ionised product, *viz.*, neutralisation, precipitation, replacement of a weak by a strong acid or base, and complex formation, may be followed by measurement of conductivity.[3] The end-point is marked by a change in the direction of the conductivity–titration curve. If the volume of a dilute solution does not change during the titration, this curve should consist, in general, of two straight lines intersecting at the end-point. In order to minimise the volume change, the titrant, preferably added from a micro-burette, should be 10—20 times as concentrated as the solution titrated; for accurate work a correction must be applied.[4] The end-point is obtained graphically, and so no special precautions need be taken in its vicinity. Solutions as dilute as 0·0001N may be titrated with reasonable accuracy provided other electrolytes are absent;[5] unless carbon dioxide can be excluded it is necessary to apply a correction in the titration of weak acids and bases.[6] To estimate the precise position of the end-point, the two conductivity lines should cut as acutely as possible, and the titrants are chosen to this end.[7] In the neutralisation of an acid of K_a about 10^{-4}—10^{-7}, a sharper angle is obtained by titrating with ammonia than with a strong base.[8] Strong and very weak (K_a *ca.* 10^{-7}—10^{-11}) acids should be neutralised by a strong base, although the intersection of the titration curves does not always occur exactly at the equivalence-point.[9] Moderately strong acids (K_a *ca.* 10^{-2}—10^{-4}) do not give sharp intersections and special methods must be used to determine the end-points;[10] one of the best is to titrate partly with ammonia and then with sodium hydroxide.[11] The presence of alcohol does not affect the end-point in acid–base titrations.[12] In precipitation reactions, errors may arise because of (*a*) solubility of the precipitate, (*b*) its speed of formation, (*c*) its uncertain composition; the first two difficulties may sometimes be overcome by the addition of alcohol,[13] and the last by titrating a hot solution.[14]

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[97] A. Petit, *Bull. Soc. chim.*, 1932, [iv], **51**, 1312; *A.*, 137.

[98] E. Müller and G. Haase, *Z. anal. Chem.*, 1933, **91**, 245; *B.*, 271; N. I. Chlopin, *Vestn. Metalloprom.*, 1932, **12**, No. 3, 74; *B.*, 432.

[99] P. Dickens and G. Thanheiser, *Arch. Eisenhüttenw.*, 1932—33, **6**, 379; *B.*, 430; W. Bohnholtzer, *Z. anal. Chem.*, 1932, **87**, 401; *B.*, 1932, 430.

[1] V. F. Stefanovski, *J. Gen. Chem.* (*U.S.S.R.*), 1931, **1**, 991; *B.*, 1932, 553; I. Tananaev, *J. Appl. Chem. Russia*, 1932, **5**, 86; *B.*, 1932, 1084.

[2] V. A. Kargin and M. I. Usanovich, *ibid.*, p. 458; *B.*, 215.

[3] I. M. Kolthoff, *Ind. Eng. Chem.* (*Anal.*), 1930, **2**, 225; *A.*, 1930, 1142.

[4] E. C. Righellato and C. W. Davies, *Trans. Faraday Soc.*, 1933, **29**, 429; *A.*, 242.

[5] See, however, G. Jander and H. Schorstein, *Angew. Chem.*, 1932, **45**, 701; *A.*, 1932, 1222.

[6] W. Poethke, *Z. anal. Chem.*, 1931, **86**, 45; *A.*, 1931, 1256.

[7] I. M. Kolthoff, *loc. cit.*, ref. (3).

[8] E. D. Eastman, *J. Amer. Chem. Soc.*, 1925, **47**, 332; *A.*, 1925, ii, 594.

[9] I. M. Kolthoff, *Z. anorg. Chem.*, 1920, **111**, 1; *A.*, 1920, ii, 420.

[10] *Idem, ibid.*

The experimental methods have been simplified by recent developments of technique. Thermionic-valve oscillators,[15] silent in operation, have replaced the induction coil, and for titrations not requiring very high accuracy A.C. mains may be used; [16] the sound in the telephones may be increased by amplifiers,[17] or the telephone can be replaced by a galvanometer in conjunction with a thermal-junction,[18] or with galena,[19] carborundum,[20] valve,[21] or copper–copper oxide [22] rectifiers. The Wheatstone bridge can be arranged so as to read directly the conductivity of the titrated solution,[23] but for many purposes the use of a bridge can be avoided; the A.C. is passed through the experimental cell and the current strength

[11] E. C. Righellato and C. W. Davies, *loc. cit.*, ref. (4).

[12] W. Poethke, *Z. anal. Chem.*, 1931, **86**, 399; *A.*, 1932, 135.

[13] I. M. Kolthoff, *ibid.*, 1922, **61**, 171; *A.*, 1922, ii, 452.

[14] H. S. Harned, *J. Amer. Chem Soc.*, 1917, **39**, 252; 1917, ii, 272.

[15] R. E. Hall and L. H. Adams, *ibid.*, 1919, **41**, 1515; *A.*, 1919, ii, 490; H. Ülich, *Z. physikal. Chem.*, 1925, **115**, 377; *A.*, 1925, ii, 671; J. W. Woolcock and D. M. Murray-Rust, *Phil. Mag.*, 1928, [vii], **5**, 1130; *A.*, 1928, 712; G. Jones and G. M. Bollinger, *J. Amer. Chem. Soc.*, 1929, **51**, 2407; *A.*, 1929, 1161; E. Götte and W. Schramek, *Z. Elektrochem.*, 1931, **37**, 820; *A.*, 1931, 1387; W. Hiltner, *Chem. Fabr.*, 1931, 389, 398; *A.*, 1931, 387; W. Muchlinsky, *ibid.*, pp. 462, 469; *A.*, 1932, 138; E. Denina and G. Sella, *Ind. chim.*, 1932, **7**, 986; *A.*, 1932, 999.

[16] W. D. Treadwell and C. Paoloni, *Helv. Chim. Acta*, 1925, **8**, 89; *A.*, 1925, ii, 595; T. Callan and S. Horrobin, *J. Soc. Chem. Ind.*, 1928, **47**, 329T; *B.*, 1929, 154; T. T. Potts, *Paper Trade Review*, 1931, **95**, 1037; *Proc. Tech. Sect. Paper Makers' Assoc.*, 1931, **12**, 156; *B.*, 1932, 177.

[17] R. E. Hall and L. H. Adams, *loc. cit.*, ref. (15); G. Jones and G. M. Bollinger, *loc. cit.*, ref. (15).

[18] G. Jander and O. Pfundt, *Z. anorg. Chem.*, 1926, **153**, 219; *A.*, 1926, 700; *Z. Elektrochem.*, 1929, **35**, 206; *A.*, 1929, 652; "Die visuelle Leitfähigkeitstitrationen," 1929; G. Jander, *Z. angew. Chem.*, 1929, **42**, 1037; *A.*, 1930, 51.

[19] G. Jander and E. Manegold, *Z. anorg. Chem.*, 1924, **134**, 283; *A.*, 1924, ii, 496.

[20] T. Callan and S. Horrobin, *loc. cit.*

[21] W. D. Treadwell and C. Paoloni, *loc. cit.*, T. Callan and S. Horrobin, *loc. cit.*; J. A. C. Teegan, *Nature*, 1930, **126**, 504; *A.*, 1930, 1375; W. Muchlinsky, *loc. cit.*

[22] F. L. Hahn, *Z. Elektrochem.*, 1930, **36**, 989; *A.*, 1931, 189.

[23] E. C. Righellato and C. W. Davies, *loc. cit.*, ref. (4).

measured by means of a galvanometer and rectifier.[24] The galvanometer readings are plotted directly on the conductivity–titration graph. The Dionic water tester has been used with success in a number of titrations.[25] Special cells have been designed,[26] and in view of the simplification of procedure, conductometric methods should find increasing applications in analytical work. The most important processes studied in recent years are the titration of: acids and bases of various strengths,[27] mixtures of acids,[28] mixtures of sodium hydroxide and carbonate,[29] salts of weak acids and bases,[30] carbonic acid,[31] phosphoric acid,[32] the salts of heavy metals,[33] phenols,[34] alkaloids,[35] anions forming sparingly soluble mercuric, silver, lead, or barium salts,[36] cations yielding slightly soluble sulphates, chromates, oxalates, ferrocyanides, ferricyanides, or nitroprussides,[37] molybdate, tungstate, and thallium,[38] ferrocyanide by zinc,[39] fatty acids,[40] zinc chloride, and cyanates.[41] S. G.

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[24] W. D. Treadwell and C. Paoloni, *loc. cit.*; T. Callan and S. Horrobin, *loc. cit.*; T. T. Potts, *locc. cit.*

[25] N. Rae, *J.*, 1931, 3143; *A.*, 1932, 135.

[26] H. T. S. Britton and W. L. German, *ibid.*, 1930, 1249; *A.*, 1930, 860; J. M. Preston, *ibid.*, 1931, 1827; *A.*, 1931, 1026.

[27] I. M. Kolthoff, *Z. anorg. Chem.*, 1920, **111**, 1; *A.*, 1920, ii, 420; E. C. Righellato and C. W. Davies, *loc. cit.*; *idem, Trans. Faraday Soc.*, 1933, **29**, 437; see also P. Hirsch, *Z. anal. Chem.*, 1926, **68**, 160; *A.*, 1926, 700.

[28] I. M. Kolthoff, *Z. anorg. Chem.*, 1920, **111**, 28; *A.*, 1920, ii, 421; E. C. Righellato and C. W. Davies, *locc. cit.*

[29] I. M. Kolthoff, *Z. anorg. Chem.*, 1920, **112**, 155; *A.*, 1920, ii, 705; M. Auméras and J. Marcon, *Bull. Soc. chim.*, 1932, [iv], **51**, 1594; *A.*, 363.

[30] I. M. Kolthoff, *Z. anorg. Chem.*, 1920, **111**, 97; *A.*, 1920, ii, 501.

[31] *Idem, ibid.*, 1920, **112**, 155; *A.*, 1920, ii, 705.

[32] *Idem, ibid.*, p. 165; *A.*, 1920, ii, 705; (Miss) J. C. Lanzing and L. J. van der Wolk, *Rec. trav. chim.*, 1928, **48**, 83; *A.*, 1929, 284.

[33] I. M. Kolthoff, *Z. anorg. Chem.*, 1920, **112**, 172; *A.*, 1920, ii, 709.

[34] *Idem, ibid.*, p. 187; *A.*, 1920, ii, 711; O. Pfundt and C. Junge, *Ber.*, 1929, **62**, 515; *A.*, 1929, 586.

[35] I. M. Kolthoff, *Z. anorg. Chem.*, 1920, **112**, 196; *A.*, 1920, ii, 781.

[36] *Idem, Z. anal. Chem.*, 1922, **61**, 229, 336, 369, 433; *A.*, 1922, ii, 581, 655, 781, 864; G. Jander, O. Pfundt, and H. Schorstein, *Z. angew. Chem.*, 1930, **43**, 507; *A.*, 1930, 1142; I. M. Kolthoff and T. Kameda, *Ind. Eng. Chem.* (*Anal.*), 1931, **3**, 129; *A.*, 1931, 699; O. Pfundt, *Angew. Chem.*, 1933, **46**, 200; *A.*, 582.

[37] I. M. Kolthoff, *Z. anal. Chem.*, 1923, **62**, 1, 97, 161, 209, 214, 216; *A.*, 1923, ii, 88, 88, 256, 260, 256, 257.

[38] E. Rother and G. Jander, *Z. angew. Chem.*, 1930, **43**, 930; *A.*, 1930, 1548.

[39] G. Jander, O. Pfundt, and H. Schorstein, *loc. cit.*

[40] G. Jander and K. F. Weitendorf, *Angew. Chem.*, 1932, **45**, 705; *A.*, 49.

[41] O. Pfundt, *ibid.*, 1933, **46**, 218; *A.*, 582.

Gas Analysis.

Micro-Gas Analysis.—This term is best restricted to processes in which a very small amount of gas is analysed, and should not be applied to those where a relatively large volume of gas is tested for minute traces of a constituent. Processes for the analysis of volumes of the order of 1 ml.[1] differ little in method from those for larger quantities; for samples of 0·1 ml. or less, however, a special technique is required. In some earlier methods[2] for quantities of this magnitude, the gas was measured at low pressures by means of a McLeod gauge; such processes are, however, being supplanted by the use of instruments of extremely simple form,[3, 4, 5, 6, 7] in which 0·02—0·1 ml. of gas is measured in a vertical or horizontal[7] graduated capillary tube of approximately 0·5 mm. bore, and transferred for absorption, through a syphon tube, to small inverted test-tubes standing in a mercury trough; the gas does not come in contact with a tap or other possible source of leak during the analysis. The gas is measured in the dry state, instead of its being saturated with water vapour, and in most of the processes,[3, 5, 6, 7] solid absorbents are used, introduced into the absorption vessels in the form of beads fused on the end of platinum wire. Oxygen is absorbed with solid phosphorus, washed with water and alcohol, and dried;[7] water vapour with fused phosphoric oxide; and ammonia with potassium hydrogen sulphate.[7] Carbon monoxide is absorbed with silver oxide (precipitated, pressed moist, and then dried; no carbon dioxide is produced).[5, 8] Where no suitable solid absorbent is available, beads of sintered glass[6] or of kaolin and ground pottery,[7] impregnated with liquid reagent, are found satisfactory; sulphuric acid, for example, is used in this way for the absorption of ethylene.[6] Combustion is effected by explosion initiated by a spark between specially designed electrodes, or, in the case of hydrogen, by heating the outside of the tube with a flame.[5] The paramount factor is the design and construction of apparatus so as to avoid gas-locks; details of such technique are given in the papers cited.[9]

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[1] *E.g.*, D. S. Chamberlin and D. M. Newitt, *Ind. Eng. Chem.*, 1925, **17**, 621; H. R. Ambler, *Analyst*, 1929, **54**, 517.

[2] I. Langmuir, *J. Amer. Chem. Soc.*, 1912, **34**, 1310; P. A. Guye and F. E. E. Germann, *J. Chim. physique*, 1916, **14**, 194; H. M. Ryder, *J. Amer. Chem. Soc.*, 1918, **40**, 1656; C. H. Prescott, *ibid.*, 1928, **50**, 3237.

[3] L. Reeve, *J.*, 1924, **125**, 1946.

[4] J. A. Christiansen, *J. Amer. Chem. Soc.*, 1925, **47**, 109; J. A. Christiansen and J. R. Huffmann, *Z. anal. Chem.*, 1930, **80**, 435.

[5] F. E. Blacet and P. A. Leighton, *Ind. Eng. Chem.* (*Anal.*), 1931, **3**, 266.

[6] F. E. Blacet, G. D. MacDonald, and P. A. Leighton, *ibid.*, 1933, **5**, 272.

[7] J. S. Swearingen, O. Gerbes, and E. W. Ellis, *ibid.*, 1933, **5**, 369.

[8] A. Gautier, *Compt. rend.*, 1898, **126**, 171.

Without personal experience, it is difficult to assess the accuracy of these methods as compared with that of macro-methods, but from some of the results given,[6] the attainable accuracy seems to be of the same order (0·1%). Manipulation, moreover, appears to be neither difficult nor slow; indeed, the latest investigators [7] find that an analysis takes less time than with the Orsat or Burrell (elaborated precision Orsat) apparatus. There is, therefore, a case for the use of micro-technique even where plenty of sample is available, but experience will be needed to decide on this point. In the Reporter's opinion, the elimination of liquid reagents is in itself likely to increase accuracy, and it is undoubtedly easier, other things being equal, to work with a small instrument and a small quantity of gas. There are, of course, some processes, *e.g.*, fractional combustion, which have not yet been made amenable to micro-technique.

Fractional Combustion Methods.—J. G. King and L. J. Edgcombe [10] have made a thorough study of the copper oxide method, and have shown that hydrogen and carbon monoxide are completely oxidised by copper oxide at 280° and methane unaffected; the carbon monoxide can be accurately determined by measuring the volume of carbon dioxide produced. This work seems to re-establish the process as a precise method after some rather discouraging results by other workers.[11] Homologues of methane are slightly attacked at 280°, and, if these are present in considerable amount, carbon monoxide should be removed by absorption, and the hydrogen oxidised at 230—250°. In a method used by the Reporter [12] for the determination of small proportions of methane (0·003% and upwards) in combustible gases, hydrogen and carbon monoxide are oxidised by copper oxide; any residual traces of these are detected and removed by a check fractional combustion with oxygen in the presence of platinum wire at very dull red heat. The methane is then burned by raising the temperature of the wire to bright yellow heat.

K. A. Kobe and E. J. Arveson [13] have investigated the use of platinised silica-gel for the catalytic fractional combustion of hydrogen and carbon monoxide; at 300° these are found to be fully oxidised, and methane unaffected. Hydrogen alone is oxidised at 100°, but at this temperature the catalyst is poisoned by carbon monoxide.

[9] Particularly ref. (5).

[10] *Fuel Research Technical Paper No.* 33, 1931.

[11] E. Ott and E. Scherb, *Z. anal. Chem.*, 1926, **68**, 238; E. Scherb, *Gas- und Wasserfach*, 1924, **67**, 391.

[12] H. R. Ambler, *Analyst*, 1931, **56**, 635.

[13] *Ind. Eng. Chem.* (*Anal.*) 1933, **5**, 110.

If this process is found to be reliable, and the catalyst to retain its activity without frequent regeneration,[14] the method is likely to be of great value for precise analysis, especially if higher paraffins are found to be unaffected.

Catalytic oxidation of carbon monoxide at ordinary temperatures, by means of metallic oxide preparations (" Hopcalite ") [15] has been applied to the design of apparatus for continuous indication of traces of carbon monoxide in air.[16] The heat produced by the oxidation of the carbon monoxide is indicated by means of a thermocouple and galvanometer graduated in terms of carbon monoxide concentration; 0·01% can readily be detected. Further processes for the determination of carbon monoxide by the iodine pentoxide method have been published.[17, 18]

Analytical Absorbents.—The use of suspensions of iodine pentoxide in oleum for the analytical absorption of carbon monoxide [19] has received further study,[20, 21] and it seems established that it is thoroughly reliable, provided that hydrocarbons other than methane be absent. Suspensions of iodine in oleum also absorb carbon monoxide but are less satisfactory.[21]

Hydrobromic acid in glacial acetic acid has been recommended for the absorption of higher olefins in the presence of ethylene; [22] and for hydrogen, a platinum preparation contained in a special pipette, in contact with sodium chlorate solution.[23] On the important and debated question of the extent of the evolution of carbon monoxide when oxygen is absorbed by alkaline pyrogallol,[24]

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[14] Compare E. Ott, *Helv. Chim. Acta*, 1924, **7**, 886; *Z. anal. Chem.*, 1926, **68**, 240; E. Scherb, *Gas- und Wasserfach*, 1924, **67**, 391.

[15] A. B. Lamb, W. C. Bray, and J. C. W. Frazer, *J. Ind. Eng. Chem.*, 1920, **12**, 213; A. B. Lamb, C. C. Scalione, and G. Edgar, *J. Amer. Chem. Soc.*, 1922, **44**, 738.

[16] *J. Sci. Instr.*, 1932, **9**, 327; *Electrician*, 1933, **111**, 309.

[17] P. Borinski and H. Murschhauser, *Chem. Fabrik*, 1932, **5**, 541; A. Bech, *Chem. Abstr.*, 1933, **27**, 5220.

[18] O. Pfundt, *Chem. Fabrik*, 1933, **6**, 69; *B.*, 265; G. Ljunggren and G. Frang, *Svensk Kem. Tidskr.*, 1932, **44**, 279.

[19] P. Schläpfer and E. Hofmann, *Monats Bull.*, 1927, **7**, 293, 349; *Chem. Zentr.*, 1929, i, 3013; *B.*, 1930, 5.

[20] P. Schläpfer and H. Ruff, *Monats Bull.*, 1929, **9**, 5; E. Ott, *Gas- und Wasserfach*, 1929, **72**, 862; 1930, **73**, 801; E. Dittrich, *Z. angew. Chem.*, 1930, **43**, 979; P. Schläpfer, *ibid.*, 1931, **44**, 170; H. A. J. Pieters, *Z. anal. Chem.*, 1931, **85**, 50.

[21] P. Schläpfer and C. Mosca, *Monats Bull.*, 1932, **12**, 205, 253, 286; *Chem. Zentr.*, 1933, i, 268.

[22] V. Sorokin, A. Belikova, and O. Bogdanova, *J. Rubber Inst., Russ.*, 1931, **5**, 26; *Chem. Abstr.*, 1933, **27**, 5680.

[23] E. Biesalski and H. Giehmann, *Angew. Chem.*, 1932, **50**, 767.

[24] See T. J. Drakeley and H. Nicol, *J. Soc. Chem. Ind.*, 1925, **44**, 457; 1929, **48**, 62.

J. S. Haldane and R. H. Makgill[25] have shown that with analyses of air in the Haldane apparatus, no measurable carbon monoxide is produced, provided the reagent (composition specified) has stood for 70 hours after being prepared, or alternatively, is heated for an hour at 100°. For the direct absorption of nitrogen, heated lithium is found satisfactory.[26]

Miscellaneous Processes.—Processes have been described for the determination of carbon dioxide in air,[27] sulphur dioxide in air,[28] hydrogen cyanide in mixtures of carbon dioxide and air,[29] small quantities of oxygen[30] and iron carbonyl.[31] The palladium test for carbon monoxide has been studied and its sensitiveness increased,[32] and the blood test, as modified by the use of the reversion spectroscope,[33] has been used for determining very small proportions of carbon monoxide.[34] The determination of ozone with potassium iodide has been further examined by R. Ruyssen,[35] and conditions determined where the titration is accurate without the use of buffer solutions. Sources of error in the determination of hydrogen have been examined by the Reporter.[36] In the explosion method, if the hydrogen content of the mixture exploded does not exceed 20%, no appreciable oxidation of nitrogen occurs. A little hydrogen may always remain unburnt; if the hydrogen content is not less than 10%, this does not exceed 0·5% of the total hydrogen. Below this limit, however, the proportion of unburnt hydrogen may be high. In catalytic combustion with heated platinum wire, oxidation of nitrogen is insufficient to produce error. The platinum wire method has been used also for the determination of small proportions of oxygen,[37] by combustion with hydrogen. If only hydrogen and inert gases are present with oxygen, the process is accurate to 0·01% on the total gas. In the presence of oxides of carbon and methane, the process is accurate to 0·1%.

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[25] *Analyst*, 1933, **58**, 378; *B.*, 737.

[26] M. Trautz and K. F. Kipphan, *Z. anal. Chem.*, 1929, **78**, 350; H. Copaux, *Bull. Soc. chim.*, 1932, **51**, 989; J. H. Severyns, E. R. Wilkinson, and W. C. Schumb, *Ind. Eng. Chem.* (*Anal.*), 1932, **4**, 357.

[27] W. M. K. Martin and J. R. Green, *ibid.*, 1933, **5**, 114; *A.*, 478; M. D. Thomas, *ibid.*, 1933, **5**, 193; L. W. Winkler, *Z. anal. Chem.*, 1933, **92**, 23; *B.*, 366.

[28] M. D. Thomas and R. J. Cross, *Ind. Eng. Chem.*, 1928, **20**, 645; S. W. Griffin and W. W. Skinner, *ibid.*, 1932, **24**, 862.

[29] H. L. Cupples, *Ind. Eng. Chem.* (*Anal.*), 1933, **5**, 50; *A.*, 243.

[30] M. Mugdan and J. Sixt, *Angew. Chem.*, 1933, **46**, 90.

[31] E. Pohland and W. Harlos, *Z. anal. Chem.*, 1932, **90**, 193; *A.*, 43.

[32] W. Ackermann, *Chem.-Ztg.*, 1933, **57**, 154; *Nature*, 1933, **131**, 441.

[33] H. Hartridge, *Proc. Roy. Soc.*, 1923, [*A*], **102**, 575; R. C. Frederick, *Analyst*, 1931, **56**, 561.

[34] See H. Hartridge, *Nature*, 1933, **131**, 654.

[35] *Natuurwetensch. Tijds.*, 1933, **15**, 125; *A.*, 921; see also A. Juliard and S. Silberschatz, *Bull. Soc. chim. Belg.*, 1928, **37**, 205; *A.*, 1928, 978.

[36] H. R. Ambler, *Analyst*, 1930, **55**, 436, 677.

[37] *Ibid.*, p. 677.

A new method for the determination of nitrous oxide has been adumbrated by L. Meyer,[38] based on the observation that when this gas is absorbed by active charcoal at temperatures above 0°, oxygen is permanently retained, only the nitrogen being removable. If such a process proves satisfactory, it will be of great value, considering the complete dearth of direct methods of determination; no details are, however, given.

L. C. McNair and H. C. Gull[39] determine combustible vapours in air by burning them in a special apparatus by means of platinum wire, and measuring the volume change by a sensitive device compensated against changes in temperature and barometric pressure. The Reporter has devised a combustion vessel for the controlled slow combustion of gases.[40] This is used in a method for the direct determination of nitrogen in combustible gases, these being burned in a stream of electrolytic oxygen, the excess of which is afterwards absorbed, together with the resulting carbon dioxide, by alkaline pyrogallol.

Other instruments which have been described are a compensator[41] for constant-volume gas burettes and a portable apparatus[42] for general gas analysis in which an accuracy of 0·1% is attained with small weight and bulk by the application of a special principle of gas-measurement. In this method both volumes and pressures are measured, the measured pressure being used to correct the volumes to standard (atmospheric) pressure. For analyses of 0·5% accuracy, the pressure measurement may be omitted. Gases can also be measured at constant volume; the volumes dealt with are about 10 ml. J. J. Fox and L. G. Groves[43] have designed a recording instrument for small traces of sulphur dioxide in flue gases; some automatic instruments for the determination of carbon monoxide have been mentioned.[16, 18]

Substances whose determination had received little attention hitherto are the vapours of lead tetraethyl,[44] amyl alcohol and acetate[45] and ethylene oxide,[46] the oxides of chlorine,[47] and the products of the thermal decomposition of phosgene.[48]

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[38] *Naturwiss.*, 1932, **20**, 791.

[39] *Analyst*, 1932, **57**, 159.

[40] H. R. Ambler, *J. Sci. Instr.*, 1931, **8**, 18; *Analyst*, 1931, **56**, 804.

[41] *Ibid.*, p. 374.

[42] *Ibid.*, p. 369.

[43] *J. Soc. Chem. Ind.*, 1932, **51**, 7; *B.*, 1932, 323.

[44] *Ministry of Health, Final Report of the Departmental Committee on Ethyl Petrol*, 1930.

Analysis of Hydrocarbon Mixtures.—Mixtures of homologous hydrocarbons, particularly paraffins, have in the past presented a very difficult analytical problem. Chemical separation is out of the question, and the usual practice has been to burn the mixed gases with oxygen, and from the data so obtained (*i.e.*, contraction, carbon dioxide produced, and oxygen consumed) to express the mixture as C_nH_{2n+2}, with an empirical value for n. A recent process which gives some information as to the identity and proportions of the different constituents which make up this average n is to allow some of the gas to diffuse out through a standard orifice and determine n before and after this process.[49] J. Dubois,[50] using the Union portable gas calorimeter,[51] determines the calorific value of gases to obtain information as to the nature of the " heavy hydrocarbons " which are usually determined together in an analysis.

The only exact method, however, for mixtures of unknown qualitative composition, or those containing more than two homologues, is separation by a physical process, such as fractionation of the liquefied gas. A process for the fractionation of complex mixtures was described in 1915 by G. A. Burrell, F. M. Seibert, and I. W. Robertson[52] and has since been improved by W. E. Stockings and G. W. Himus;[53] the introduction, however, of vacuum-jacketed fractionating columns[54] has made the separation almost as simple as the separation of liquids in an organic laboratory. The various constituents distil over almost completely separated, and are identified by their boiling points and measured by collection of each constant-boiling fraction in a previously evacuated vessel of known volume, connected to a manometer. For binary and ternary mixtures of known qualitative composition, a " short-cut " method has been devised for further speed and simplification;[55]

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[45] I. M. Korenman, *J. Appl. Chem. Russ.*, 1931, **4**, 940; *A.*, 1932, 632.

[46] W. Deckert, *Angew. Chem.*, 1932, **45**, 559; *B.*, 1932, 1010.

[47] J. W. T. Spinks, *J. Amer. Chem. Soc.*, 1931, **53**, 3015.

[48] A. Stock and W. Wustrow, *Z. anorg. Chem.*, 1931, **195**, 129; *A.*, 1931, 326.

[49] R. A. Baxter and L. J. Beckham, *J. Amer. Chem. Soc.*, 1933, **55**, 3926.

[50] *Przemyst Chem.*, 1931, **15**, 390; *B.*, 1932, 247.

[51] See A. Blackie, *J. Sci. Instr.*, 1930, **7**, 84.

[52] *U.S. Bur. Mines, Tech. Paper No.* 104, 1915.

[53] " Fuel Testing," 1932, p. 195.

[54] F. E. Frey and W. P. Yant, *Ind. Eng. Chem.*, 1927, **19**, 21, 492; H. S. Davis, *Ind. Eng. Chem.* (*Anal.*), 1929, **1**, 61; H. J. Lucas and R. T. Dillon, *J. Amer. Chem. Soc.*, 1928, **50**, 1460; W. J. Podbielniak, *Ind. Eng. Chem.* (*Anal.*), 1931, **3**, 177; 1933, **5**, 119, 172; W. E. MacGillivray, *J.*, 1932, 941.

[55] R. Rosen and A. E. Robertson, *Ind. Eng. Chem.* (*Anal.*), 1931, **3**, 284.

the temperatures are noted at which certain definite percentages of the total gas have been evaporated off under standardised conditions, and from these data the percentages of the constituents are obtained from empirically constructed graphs. For simpler mixtures of hydrocarbons [56] and for fractionation processes to be used in conjunction with chemical analyses,[57] simpler processes have been described.

A further method for complex hydrocarbon mixtures, which seems to give accurate separation, is selective absorption by cooled charcoal.[58] The constituent gases are desorbed successively from the charcoal and can be collected separately; the changes in the composition of the emergent gases are observed by means of a gas-interferometer.[59] G. Kuhn [60] has described a somewhat similar process, using silica-gel.

Miscellaneous Physical Methods of Analysis.—The year 1933 has seen the appearance of an authoritative text book [61] on the thermal conductivity method. This method is of great and increasing application, particularly for control work in technical processes, since it is usually automatic and recording, and is ideally suited to "flow" analyses. The "viscosity-effusion bridge" [62] is an instrument with a wide field of possible application, working on the principle of the relation between the density and viscosity of a gas. Small differences in this relation between the gas under test and a comparison gas are indicated on an oil-manometer. The method is particularly sensitive for gases of high density and low viscosity, such as organic vapours; for instance, 1% of hexane vapour in air produces a movement of 150 mm. on the manometer. The design of the instrument allows it to be used with corrosive gases.

M. Lambrey [63] finds that some bands in the absorption spectrum of nitric oxide are greatly strengthened by the presence of another gas, and can thus detect nitric oxide at a partial pressure of 0·002 mm. in one atmosphere of hydrogen. E. J. B. Willey and S. G. Foord,[64] using the potassium photoelectric cell, which is most sensitive in that region of the spectrum where absorption by nitrogen peroxide is strongest, are able to determine 0·001% of this gas. R. Ruyssen [65] uses the potassium photoelectric cell for the determination of ozone. Researches by A. Gatterer [66] indicate the feasibility of quantitative determination of some gases by emission spectra.

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[56] E. M. J. Mulders and F. E. C. Scheffer, *Rec. trav. chim.*, 1930, **49**, 1057; *A.*, 1931, 54; C. A. L. Horstmann and F. E. C. Scheffer, *Rec. trav. chim.*, 1932, **51**, 153; *A.*, 1932, 247; O. J. Walker and S. N. Shukla, *J.*, 1931, 368.

[57] H. S. Davis and J. P. Daugherty, *Ind. Eng. Chem.* (*Anal.*), 1932, **4**, 193.

[58] P. Schuftan, "Gasanalyse in der Technik," 1931, p. 69; see also E. Berl and O. Schmidt, *Z. angew. Chem.*, 1923, **36**, 247.

[59] (Lord) Rayleigh, *Proc. Roy. Soc.*, 1896, **59**, 201.

[60] *Z. angew. Chem.*, 1931, **44**, 757; *B.*, 1932, 7.

[61] H. A. Daynes, "Gas Analysis by Measurement of Thermal Conductivity," 1933.

[62] I. Fagelston, *Brit. Pat.*, 330799 (1929); *B.*, 1930, 799; *Ind. Chem.*, 1932, **8**, 57.

[63] *Compt. rend.*, 1931, **139**, 857.

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[64] *Proc. Roy. Soc.*, 1932, [*A*], **135,** 166.

[65] *Natuurwetensch. Tijds.*, 1933, **15,** 6; *Bull. Acad. roy. Belg.*, 1932, [v], **18,** 1085; *A.*, 362.

[66] *Physikal. Z.*, 1932, **33,** 64.

BIOCHEMISTRY.

A SECTION has been devoted this year to certain aspects of the biochemistry of bacteria. The extreme diversity of the chemical activity of these organisms renders impossible any approach to a comprehensive review of recent investigations. The more practical aspects of bacteriology in relation to industry, pathology, agriculture, sanitation, etc., receive attention elsewhere. It has seemed more appropriate to consider certain selected topics, which by reason of their fundamental or theoretical character are suitable for inclusion here. Moreover, since no reference to bacteria has appeared for some time in these Reports, the period under consideration has been extended to cover the last three or four years. A short section on algæ has similarly been introduced.

In the section dealing with animal biochemistry the subjects reviewed this year are the highly important new fermentation schemes of Embden and Meyerhof, deaminisation by surviving tissues, metabolic aspects of methionine, *vitamin A*, *vitamin C (ascorbic acid)*, the physiology of vitamin B_1, carcinogenesis by pure hydrocarbons, synthetic œstrogenic substances, the œstrin group, and the new group of the *flavin pigments*. The more chemical aspects of the subjects italicised are dealt with in the aliphatic division of the organic chemistry report.

PLANT BIOCHEMISTRY.

Biochemistry of Certain Bacteria.

The Nitrogen Assimilation of Azotobacter.—The relationship between the nature of the nitrogen assimilation process and the growth of these important organisms has presented a fascinating problem to both the bacteriologist and the agriculturalist. It has long been recognised that in the presence of nitrates the fixation of free nitrogen by *Azotobacter* is retarded or entirely prevented. The more precise information of the detail of this effect which has become available during the last two or three years is to a large extent due to the work of D. Burk and H. Lineweaver. Their earlier investigations [1] showed that the addition of small but increasing amounts of combined nitrogen to otherwise nitrogen-free media rapidly reduced the amount of elementary nitrogen fixed. Fixation ceased altogether when the medium contained 0·5 mg. of available N per c.c. The growth and respiration rates of the organism also increased rapidly with the supply of combined-nitrogen, reaching a maximum with 0·5—1·0 mg. of N per c.c. and declining slowly as this value was exceeded. As far as could be ascertained, the principal physiological functions of the bacteria were unaltered whether the assimilated nitrogen was free or combined. The nitrogen content of the dry matter of the cells was likewise unaffected.

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[1] *J. Bact.*, 1930, **19**, 389; *A.*, 1930, 1219.

It would appear that for normal metabolic processes *Azotobacter* utilise combined nitrogen if available and will resort to fixation only when the alternative source fails. This view is confirmed, and more light thrown on the relative assimilability of various nitrogenous compounds by J. E. Fuller and L. F. Rettger.[2] The effect of a range of nitrogenous compounds varying in complexity from simple nitrates and ammonium salts to simple amides and amino-acids (urea, glycine, aspartic and glutamic acids) and more complex compounds such as tyrosine, nucleic acid, etc., on nitrogen fixation by, and the reproduction of, *Azotobacter* was compared with those in cultures from which all combined nitrogen was excluded. In general, the simpler compounds were the more easily assimilated, produced the greater growth increases, and, at the same time, caused the heavier reduction in the amount of free nitrogen fixed. Similar effects were observed by L. G. Thompson.[3] The clear differentiation between the course of N fixation and the growth process in *Azotobacter* is further emphasised in the nutritional requirements. Thus in media containing the customary minerals (K, Mg, PO_4''', SO_4'', etc.) and combined nitrogen little calcium seems necessary for optimum growth and normal metabolism.[4] During the fixation process calcium is necessary in considerable amount and becomes an important factor controlling the amount of nitrogen fixed.[5] The interesting point is brought out by this investigation that strontium, but no other element, can replace calcium in this function.[5, 6]

The first product of nitrogen fixation so far identified is ammonia, and this appears only when an adequate energy (carbohydrate) source is available. If the organism is supplied with combined forms of nitrogen, these are decomposed with the production of ammonia, which is then utilised. The deamination process apparently occurs only in the absence of carbohydrates (S. P. Kostytschev and A. Scheloumov).[7]

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[2] *Soil Sci.*, 1931, **31**, 219; *B.*, 1931, 557.

[3] *J. Agric. Res.*, 1932, **45**, 149; *A.*, 1932, 1169.

[4] M. Schröder, *Zentr. Bakt. Par.*, 1932, II, **85**, 177; *A.*, 1932, 306.

[5] D. Burk and H. Lineweaver, *Arch. Mikrobiol.*, 1931, **2**, 155; *A.*, 1931, 1334.

[6] D. Burk, *Proc. 2nd Internat. Cong. Soil Sci.*, 1932, **3**, 67; *A.*, 96.

The examination of the effects of varying partial and total pressures of oxygen and nitrogen on the fixation process, by Burk,[8] discussed in an earlier Report,[9] initiated a series of investigations of the mechanism of the stimulatory action of humus, and later, of other substances on the activities of *Azotobacter*. In experiments on the respiratory exchange, K. Iwasaka [10] showed that the reproductive process is associated with a steady increase in the respiratory rate, whereas the fixation process takes place with constant respiratory conditions. A low oxygen pressure favours fixation and inhibits growth, and respiratory activity. Humic matter increases the respiration rate. The fixation of nitrogen is also accelerated by molybdenum salts (Na_2MoO_4),[11, 12] but the mechanism of the stimulation differs from that produced by soil extracts. Both materials increase the proportion of nitrogen fixed per unit of sugar consumed, but neither affects the ratio, nitrate assimilated : sugar consumed. Soil extract accelerates the growth rate of the organism, and in this respect, is effective whether free or combined nitrogen is being assimilated. The action of the molybdate, however, is confined to increasing the efficiency of the fixation process. That the growth-accelerating effect is a function of some organic constituent of soils is confirmed by the observation that the ash of soil extracts acts in a precisely similar manner to, and with approximately the same intensity as, the sodium molybdate. The activity of the latter apparently differs from that of uranium (and in some cases of thorium), which, as previously reported by K. Hirai,[13] stimulates both nitrogen fixation and growth. The action of humus is stated by J. Voicu and E. Lungulescu [14] to depend on its influence over the utilisation of energy materials by *Azotobacter* as well as on the actual fixation process. Thus, small amounts of humus accelerate the oxidation of sucrose but retard that of glucose. Larger proportions in general retard oxidation to extents which vary with the nature of the carbohydrate present.

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[7] *Z. physiol. Chem.*, 1931, **198**, 105; *A.*, 1931, 986; *Bull. Acad. Sci. U.R.S.S.*, 1931, 661; *A.*, 1931, 1459.

[8] *J. Physical Chem.*, 1930, **34**, 1174; *A.*, 1930, 1068.

[9] *Ann. Reports*, 1930, 242.

[10] *Biochem. Z.*, 1930, **226**, 32; *A.*, 1930, 1622.

[11] H. Bortels, *Arch. Mikrobiol.*, 1930, **1**, 333; *A.*, 1931, 1095.

[12] L. Birch-Hirschfeld, *ibid.*, 1932, **3**, 341; *A.*, 1932, 1169.

[13] *Proc. 1st Internat. Cong. Soil Sci.*, 1928, **3**, 154.

[14] *Bul. Chim. Soc. Romåne*, 1930, **12**, 71, 82; *A.*, 1930, 1478.

In a further investigation, Burk, Lineweaver, and G. K. Horner[15] associate the stimulatory action of humus with its iron constituents, since artificial iron-free humus is without action. Moreover the iron salts of certain organic acids (citrate, tartrate, malate) and, to a less extent, ferric sulphate may produce similar effects, the order of efficiency being humus $>$ organic salts of iron $>$ ferric sulphate. Under cultural conditions such that natural humus fails to stimulate, the iron salts are also ineffective. It is indicated that the maintenance of an appropriate proportion of soluble iron in the medium is an important factor in the production of stimulative effects.

No confirmation was obtained by these workers of theories, frequently expressed, that the effect of humus results from its supposed action in increasing the availability of nutrient materials, in detoxicating metabolic products, or in improving the physical condition of the substrate. Burk's "iron" theory falls into line with observations of many early workers and with that of J. Olsen,[16] who ascribed the activity of Bottomley's "Bacterised peat" to the presence of iron compounds rather than to that of auximones.

Bacterial Decomposition of Sugars and their Derivatives.—The fermentation of various sugars has long formed the basis of tests used in characterising bacterial species. The consideration of fermentability by bacteria as a property of sugars which might be correlated with molecular structure is less commonly discussed. Bacteria as a class exhibit a specificity in this respect which is well defined with regard to individual sugars, but less easy to elucidate in reference to groups of sugars having common structural characteristics. An interesting variation of this theme is provided by the work of A. I. Kendall and C. E. Gross[17] in which the relative ease of fermentability of sugars is compared with that of their corresponding simple derivatives. Thus, while glucose is in general more readily fermented than mannose, the reduction products sorbitol and mannitol show the reverse order of fermentability. Oxidation of glucose to gluconic acid does not greatly restrict its utilisation by bacteria, whereas mannonic acid is attacked by relatively few organisms. The simple glucosides were rarely utilised, β-methylglucoside being more generally attacked than α-methylglucoside. α-Methylmannoside was very resistant. Alkylated sugars such as the methyl and *iso*propylidene derivatives of glucose, fructose and mannose, tetramethyl mannose, and γ-trimethyl xylose were rarely, if at all, acted on by bacteria. Investigations of a somewhat similar character are more recently recorded by S. A. Koser and

[15] *Soil Sci.*, 1932, **33**, 413, 455; *B.*, 1932, 782.

[16] *Compt. rend. Trav. Lab. Carlsberg*, 1930, **18**, 1; *B.*, 1930, 434.

[17] *J. Infect. Dis.*, 1930, **47**, 249; *A.*, 1931, 264.

F. Saunders.[18] A series of simple derivatives, selected as retaining the essential spatial arrangement of atoms, were subjected to the action of a series of bacterial species, and, incidentally, of two yeasts. Here again the refractory character of the glucosides is shown, *d*-α-methylmannoside, *l*-β-methylarabinoside, and *d*-β-methylxyloside being unattacked by any of the organisms which fermented the corresponding simple sugars, and α-methylglucoside being fermented only in a few instances. On the other hand the introduction of the methyl group into the direct carbon chain as in rhamnose and fucose did not markedly reduce fermentability. Of the heptoses, α-glucoheptose and α-glucoheptulose were not utilised by any of the bacteria examined. The hexose, sorbose, having a similar spatial arrangement to α-glucoheptulose, was fermented only by a few species. Glucosamine and gluconic acid were attacked by the majority of glucose-fermenting organisms, though not always with equal readiness. It is significant that neither compound was acted on by the yeasts. The sulphur derivative, glucose ethyl mercaptal, and the acetyl derivatives of glucose and xylose proved unfermentable. The relative ease of fermentation of glucosamine is also recorded by F. Lieben and L. Löwe,[19] and the resistant character of several glucosides towards certain organisms which attack the simple sugars by S. Forssman.[20] In another paper, S. A. Koser and F. Saunders[21] show that a number of organisms ferment *l*-arabinose more readily than the *d*-form, although in a few cases the *d*- but not the *l*-form was utilisable. It is generally indicated that the spatial arrangement of atoms or the length of the carbon chain is by no means always a controlling factor in the fermentability of sugars by bacteria, even when the activities of a single species only are considered.

Production of Acetic Acid by Bacteria.—The very varied and often complex transformations brought about by bacteria between carbohydrates, alcohols, acids and the intermediate products, together with their control by the adaptation of cultural conditions to favour or inhibit the activity of individual bacterial enzymes, form the subject of an ever increasing number of investigations. In this, as in all other forms of the biochemical changes in bacteria, the importance of small variations in the primary or secondary nutrients, of the chemical form in which these are supplied, of the temperature, hydrogen-ion concentration and oxidation-reduction potential of the media, of respiratory relationships and of the stage of development of the cultures is repeatedly emphasised. Considerable attention attaches to the mechanism of the production of acetic acid, more especially to the final stage, aldehyde ⟶ acid.

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[18] *J. Bact.*, 1933, **25**, 32; *A.*, 639; also *ibid.*, p. 475.

[19] *Biochem. Z.*, 1932, **252**, 70; *A.*, 1932, 1066.

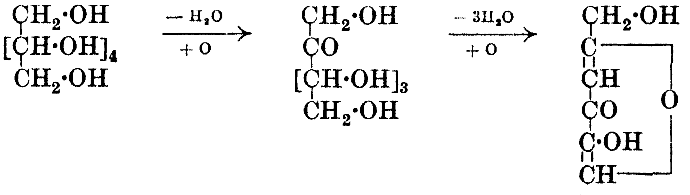
[20] *Ibid.*, 1933, **264**, 231; *A.*, 1083.

[21] *Proc. Soc. Exp. Biol. Med.*, 1932, **30**, 218; *A.*, 1932, 1206.

The dismutation theory initiated by Neuberg and Windisch in 1926 postulated the change of two molecules of aldehyde to one molecule of acid *plus* one molecule of alcohol. The latter is further attacked to produce more aldehyde, thus obscuring the true course of the change, when examined analytically.

Later H. Wieland and A. Bertho[22] presumed the direct dehydrogenation of aldehyde to be the dominant reaction, $CH_3{\cdot}CHO$ [or $CH_3{\cdot}CH(OH)_2$] $\xrightarrow{-\mathrm{H}} CH_3{\cdot}CO{\cdot}OH + H_2O$. The dehydrogenation of *iso*propyl alcohol completely to acetone is cited as a parallel action.[23] Further confirmation of the dismutation theory was furnished by E. Simon,[24, 25] who established the occurrence of a keto-aldehyde mutase in a number of species of acetic acid bacteria. K. Tanaka[26] considered the dismutation and dehydrogenation of acetaldehyde as two phases of activity of the same enzyme. Dehydrogenation with oxygen as the hydrogen-acceptor is more rapid in acid than in neutral media, the reverse being the case with dismutation. That dismutation can take place under aërobic conditions has further been established by Simon.[27]

Kojic Acid.—Certain species of acetic acid bacteria which produce gluconic acid from glucose, also yield kojic acid from fructose or mannitol. Among these are varieties of *B. hoshigaki* and, less active in this respect, *B. xylinoides*. According to T. Takahashi and T. Asai[28] the acid is formed only from fructose and mannitol, not from compounds containing less than six carbon atoms. The mechanism is represented as a progressive oxidation.



Kojic acid

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[22] *Annalen*, 1928, **467**, 95; *A.*, 1929, 219; also A. Bertho and K. P. Basu, *ibid.*, 1931, **485**, 26; *A.*, 1931, 394.

[23] A. Bertho, *ibid.*, 1929, **474**, 1; *A.*, 1929, 1492.

[24] *Biochem. Z.*, 1930, **224**, 253; *A.*, 1930, 1477.

[25] C. Neuberg and E. Simon, *ibid.*, 1932, **253**, 225; *A.*, 1932, 1169.

[26] *Acta Phytochim.*, 1931, **5**, 239; *A.*, 1932, 94.

[27] *Biochem. Z.*, 1931, **243**, 401; *A.*, 1932, 196.

[28] *Proc. Imp. Acad. Tokyo*, 1932, **8**, 364; *A.*, 189; also *Zentr. Bakt. Par.*, 1933, **II**, **88**, 286; *A.*, 1206.

It is of interest that kojic acid production by *Aspergillus* takes place from simple compounds by an entirely different process (see p. 318).

Sulphur Bacteria.—Some brief reference seems appropriate to this widely distributed class of organisms, which are characterised by the utilisation of relatively large proportions of elementary sulphur or its simple compounds.

Only a very small percentage of the assimilated sulphur is required for purely nutritional purposes; the major part serves in most cases as an agent rendering available to the organism energy from other sources. The importance of these organisms in natural waters and water supplies, in sanitation, and in their relation to soil fertility is well known. More recently their significance in geological process is being explored. The possibility is also indicated that certain classes of sulphur bacteria are associated with, if not definitely concerned in, some forms of stone decay (Paine, *et al*).[29]

Apart from these more specific activities, perhaps the chief point of recent fundamental interest is the elucidation of the complex relationship between the assimilation of hydrogen sulphide and the respiratory process in these organisms. This relationship is somewhat obscured at times by the apparent ability of the bacteria to adopt an alternative metabolic process—so-called "pleoenergism."[30] Many instances are recorded in which the normal development of the bacteria occurs in the complete absence of sulphur; *e.g.*, the purple sulphur bacteria grow under anaërobic conditions and in the presence of organic matter without any source of oxidisable sulphur and in this condition utilise radiant energy.[31, 32]

The final product of oxidation of sulphur under normal conditions is sulphate, but the process occurs in stages which include the formation of thiosulphate, thionic acids,[33] and sulphite. Intermediate-stage oxidations may be intensified by use of particular species or by variation of growth conditions. As is to be anticipated, the reaction of the medium is an important factor influencing the nature of the changes, and is utilised by some workers as a basis of classification. The particular stage or type of oxidation which is dominant in media of different reaction serves to distinguish a number of main groups of organisms.[34] For more detailed classification of the increasing number of species isolated, morphological characters, pigmentation, and the presence or otherwise of sulphur accumulations in the cells are considered.

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[29] S. G. Paine, F. V. Linggood, F. Schimmer, and T. C. Thrupp, *Phil. Trans.*, 1933, *B*, **222**, 97; *B.*, 1933, 628.

[30] "Sulphur Bacteria," D. Ellis (Longmans), p. 47.

[31] C. B. van Niel, *Arch. Mikrobiol.*, 1931, **3**, 1; *A.*, 1932, 884.

[32] F. M. Muller, *ibid.*, 1933, **4**, 131; *A.*, 1207.

[33] Penta- and tetra-thionic acids were isolated from soil cultures by G. Guittonneau and J. Keilling (*Compt. rend.*, 1932, **195**, 679; *B.*, 1932, 1128).

[34] I. P. Lange-Pozdeeva, *Arkh. Biol. Nauk*, 1930, **30**, 189; *A.*, 1930, 1622.

According to van Niel[35] the development of the purple and green sulphur bacteria is largely controlled by the concentration of hydrogen sulphide in the medium and in turn by its reaction. The metabolism is represented as a true photosynthetic process conforming to the equation $CO_2 + 2H_2S = CH_2O + H_2O + 2S$. The sulphur is deposited within or without the cells and in turn reduces more carbon dioxide; the complete equation becoming $2CO_2 + H_2S + 2H_2O \longrightarrow 2CH_2O + H_2SO_4$.

In the absence of sulphur the purple organisms utilise salts of organic acids (lactate, pyruvate, acetate, malate, succinate, etc.). The work of F. M. Muller (*loc. cit.*) indicates that the preliminary transformation of other acids to pyruvic acid is an essential step in the building up of cell constituents. In this case also the process may be regarded as a particular instance of the general photosynthetic rule. In another paper[36] Muller shows the similarity between the carbon assimilation of the red sulphur bacteria exposed to light and that of the higher plants. In the presence of hydrogen-donors the organisms reduce carbon dioxide to formic acid and thence to formaldehyde. The red pigment is closely allied to carotene and xanthophyll and appears to play a part in the assimilatory function of these bacteria, similar to that of chlorophyll in plants.

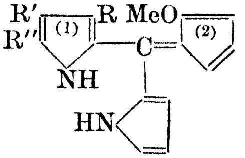
Carotenoid pigments are absent from the green sulphur bacteria, and in this species reduction of carbon dioxide occurs only in the presence of hydrogen sulphide as a hydrogen-donor. Carotenoids are associated with the utilisation of less active hydrogen-donors (*e.g.*, water) than hydrogen sulphide.

In a recent monograph D. Ellis (*op. cit.*) gives a fairly comprehensive review of the morphology and chemical activities of the sulphur bacteria.

Pigmentation and Luminescence in Bacteria.—Although the formation of colour in bacterial cultures frequently serves a useful purpose in the identification or selection of organisms, little information is available as to the nature of the pigments, their formation or purpose. The literature of the current year indicates a rising interest in this aspect of bacterial biochemistry, and a brief reference to recent investigations seems desirable here. The very definite pigments of the sulphur bacteria (see above) have been examined spectrophotometrically but of their chemical composition not very much is known. The red pigment of *B. prodigiosus* has

[35] *Loc. cit.* [36] *Chem. Weekblad*, **1933, 30**, 202; *A.*, **429.**

been more extensively studied. The production of the pigment is largely influenced by growth conditions, particularly the nature of the carbon and nitrogen sources, and the reaction of the medium.[37] W. Moycho[38] indicates that the pigment is produced during autolysis of the cells in the presence of oxygen, and undergoes a colour change (red ⟶ yellow) at p_H 8·0 approx. In a series of papers F. Wrede[39] and colleagues describe the isolation and examination of the pigment *prodigiosin*, to which is ascribed the structure :



The position of the methoxy- group in ring (2) is uncertain. $R + R' + R'' = C_6H_{15}$.

An apparent inverse relationship between the active growth of bacteria and the formation of pigment is shown in an examination of Grassberger's bacillus by G. Sandor and G. Rougebief.[40] In suitable media having a neutral or alkaline reaction the organism grows rapidly, but for some time is colourless. When acid metabolic products have accumulated to lower the p_H of the medium sufficiently, pigmentation is apparent. On the other hand, when the organism is grown in slightly acid media, the red colour is apparent throughout, but the culture develops only very slowly.

The isolation of a highly toxic pigment from bacteria developing on coconut products is described by A. G. van Veen and W. K. Mertens.[41] The yellow substance (m. p. 200°) is dialysable, amphoteric, and has a high nitrogen content. The minimal lethal dose when administered intraperitoneally to rats is less than 0·005 mg.

The dependence of pigmentation on cultural conditions is demonstrated in a number of cases. For instance, S. Arakawa[42] in an examination of *Azotobacter* shows that, whereas *A. chroococcum* and *A. vinelandii* produce pigment in media containing the simple sugars, only the former organism is coloured when the carbon source supplied is inulin, dextrin, or starch. In both cases the addition of potassium nitrate as a nitrogen source intensifies pigmentation. Similarly, in the case of organisms producing fluorescent pigments, F. R. Georgia and C. F. Poe[43] have shown that pigment production necessitates the presence in the media of magnesium, phosphates, and sulphates. Quite small proportions of these suffice, but the organisms are sufficiently sensitive to be utilised to detect, by their fluorescence, the presence of very small amounts of these essential ions. The same organisms are also very sensitive to the nature of the nitrogen supply, different samples of peptone producing unexpectedly large variations in pigmentation.[44]

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[37] G. Gorbach, *Zentr. Bakt. Par.*, 1929, II, **79**, 26; *A.*, 1930, 1219.

[38] *Compt. rend.*, 1930, **191**, 497; *A.*, 1930, 1478.

[39] F. Wrede and O. Hettche, *Ber.*, 1929, **62**, [*B*], 2678; *A.*, 1929, 1469; F. Wrede, *Z. physiol. Chem.*, 1932, **210**, 125; *A.*, 1932, 1043; F. Wrede and A. Rothhaas, *ibid.*, 1933, **215**, 67; 1933, **219**, 267; *A.*, 516, 1172.

[40] *Bull. Soc. Chim. biol.*, 1933, **15**, 415; *A.*, 640.

[41] *Proc. K. Akad. Wetensch. Amsterdam*, 1933, **36**, 666; *A.*, 1206.

[42] *Tottori Agric. Coll. Sci. Papers* (10th Anniv.), 24; *A.*, 1932, 652.

A similarly intimate relationship apparently exists between nutrient conditions and light emission by several luminescent bacteria. The work of F. Fuhrmann[45] shows that among mineral nutrients necessary to *P. radians*, both anions and cations of alkali halides contribute separate effects to the intensity of the light produced. Various sugars increase luminosity not only in actual intensity but in the rate of increase to maximum intensity and the subsequent decline. These effects differ with the nature of the sugar used and are modified to different extents by variations in the sodium chloride concentration of the medium. The organism can develop anaërobically, but free oxygen is necessary for luminescence. Light production and cell multiplication are apparently unrelated processes. A. Mudrak,[46] in an examination of several species of luminous bacteria indicates that, while light emission occurs only in the presence of free oxygen, the organisms can, in some instances, utilise sodium nitrate and chlorate as sources of respiratory oxygen. Further, these bacteria can tolerate sodium and potassium chlorates (the former up to 9%) or sodium thiosulphate in considerable proportions, but growth is checked by sodium bromate, iodate or perchlorate and by potassium iodate. As sources of nitrogen the nitrates of potassium and ammonium, urea, and tyrosine were unsatisfactory. Glycine, asparagine, and aspartic acid were utilisable, although in the case of the last-named, only the amino-nitrogen was attacked. An instance of apparently normal development in the absence of dissolved nitrogen suggests the possibility of the fixation of atmospheric nitrogen. Sodium is an essential element for the growth of all species.

S. E. Hill[47] describes the effects of ammonia and of fatty acids in destroying the luminescence of *B. fischerei*. This action is largely due to actual penetration of the cell wall, and subsequent cytolysis. At a given p_H in the medium the loss of luminescence, brought about by fatty acids, increased in the order of the series, valeric ⟶ formic acids. In certain ranges of p_H, the cytolysis occurring on exposure to 0·5M-solutions of ammonium salts of the fatty acids increased with the molecular weight of the acid.

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[43] *J. Bact.*, 1931, **22**, 349; *A.*, 1932, 198.
[44] *Ibid.*, 1932, **23**, 135; *A.*, 1932, 430.
[45] *Monatsh.*, 1932, **60**, 69, 414; *A.*, 1932, 652, 1065.
[46] *Zentr. Bakt. Par.*, 1933, II, **88**, 353; *A.*, 1334.
[47] *J. Cell. Comp. Physiol.*, 1932, **1**, 145; *A.*, 1932, 1290.

Algæ.

The chemistry of algæ receives relatively small but persistent attention from research workers, and since little reference has been made to the subject in recent Reports a brief statement of certain points arising during the past two or three years is included here. Our knowledge of the biochemistry of algæ is of a somewhat fragmentary character. Probably most consideration has been given to the nature of algæ pigments. The elucidation of metabolic process is to a considerable extent restricted to the examination of the commoner carbonaceous and nitrogenous constituents of the tissues. It is characteristic of the majority of algæ that they contain negligible amounts of sugars, the more persistent stage of carbon metabolism being represented by the sugar alcohols, mannitol, sorbitol, and dulcitol.[48, 49] According to Haas and Hill (*loc. cit.*) the formation of sugars in certain marine algæ is a much slower process than their subsequent conversion into alcohols, although the presence of certain sugars is definitely recorded, especially from samples obtained during the summer months.[50, 51]

Two sugar derivatives, algin and laminarin (or laminaroloside) are very generally distributed in algæ, the latter substance appearing in maximum quantities in the summer period. The laminarin content of *Laminaria* appears to be closely related to sea temperature and the amount of sunshine.[52] Laminarin yields only glucose on hydrolysis and is probably a condensation product of the formula $(C_6H_{10}O_5)_{6 \text{ or } 7}$. Algin is variously described as a glucoside containing a glycuronic acid residue[53] and as a mixed calcium–magnesium–aluminium salt of an acid resembling pectic acid.[54] The oxidation product, alginic acid, yields mannuronic acid on hydrolysis and monosaccharic acid on oxidation. It occurs only to a limited extent in algæ.

In an examination of the fatty constituents of seaweeds Haas

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[48] H. Colin and P. Ricard, *Compt. rend.*, 1930, **190**, 1514; *A.*, 1930, 1072.

[49] P. Haas and T. G. Hill, *Biochem. J.*, 1931, **25**, 1470; *A.*, 1932, 101; *Ann. Bot.*, 1933, **47**, 55; *A.*, 436.

[50] H. Colin and E. Guéguen, *Compt. rend.*, 1930, **190**, 884; *A.*, 1930, 825.

[51] *l*-Fucose and *d*-mannose isolated from sea weeds; R. H. F. Manske, *J. Biol. Chem.*, 1930, **86**, 571; *A.*, 1930, 825.

[52] P. Ricard, *Bull. Soc. Chim. biol.*, 1931, **13**, 417; *A.*, 1931, 883.

[53] H. Colin and P. Ricard, *ibid.*, 1930, **12**, 1392; *A.*, 1931, 535.

[54] J. Giral, *Anal. Fis. Quim.*, 1929, **2**, 144; *A.*, 1930, 259.

and Hill (*loc. cit.*, 1933) show that, although all species examined contain very similar fats, the more exposed species have, in general, a higher proportion of fat and also their fats are of lower iodine value. The unsaponifiable fraction of the fats tends also to become greater with increasing depth of average immersion of the species.

In the same communication is described the distribution of certain nitrogenous compounds. Again the influence of immersion is apparent. In most cases a high total-nitrogen content is associated with a relatively low proportion of fat. Ammonia occurs in all submerged species and rarely in those exposed. In the latter, amide-nitrogen predominates over amino-nitrogen, whereas in submerged plants the order is reversed. An octapeptide of glutamic acid is recorded in *Phæophyceæ* and also in *Pelvetia canaliculata*,[55] and methylamine and trimethylamine in a number of species by R. Kapeller-Adler and F. Vering.[56] In no case was dimethylamine detected. The presence of nitrates in a number of green algæ is shown by S. Suneson.[57] Many brown and some red species do not accumulate nitrate.

The pigments of certain red algæ have been the subject of much investigation in recent years, and much of our present knowledge is due to the work of R. Lemberg, who, from the chromoproteins phycoerythrin and phycocyan, obtained the corresponding true pigments, which he named phycoerythrobilin and phycocyanobilin. He subsequently established their close relationship with the bile pigments.[58] The chromoproteins contain approximately 2% of the true pigments, which resemble in many properties magnesium-free chlorophyll, and occur in the algæ in proportions which vary somewhat with environmental conditions. The proteins of the two compounds apparently are not identical.

Growth and Metabolism of Moulds.

Further investigations of the rôle of zinc in the growth of moulds[59] have been reported this year. A direct relationship between the zinc content of a number of fungi and their nucleolytic power is indicated by M. Mousseron and P. Fauroux.[60] Where this value exceeds 100 mg. of zinc per kilo. of dry matter, the organisms are hæmolytic. The repeatedly observed inhibitory action of zinc salts on sporulation in *Aspergillus niger* is accompanied by modifications in the metabolic and structural chemistry of this mould.[61] The addition to a sugar medium of 0·01% zinc sulphate resulted in increased utilisation of sugar and greater production of citric acid. The hemicellulose contents and the proportions of ether— and cold water—soluble matter of the mycelium were increased and that of lignin was lowered. In its stimulative effect on vegetative growth in fungi zinc is associated with the " growth substance-B," probably acting as a co-catalyst of growth.[62]

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[55] P. Haas and T. G. Hill, *Biochem. J.*, 1931, **25**, 1472; *A.*, 1932, 101.

[56] *Biochem. Z.*, 1931, **243**, 292; *A.*, 1932, 204.

[57] *Z. physiol. Chem.*, 1932, **204**, 81; 1933, **214**, 105; *A.*, 1932, 314; 1933, 437.

[58] *Annalen*, 1928, **461**, 46; 1930, **477**, 195; *A.*, 1928, 533; 1930, 488. With G. Bader, *Naturwiss.*, 1933, **21**, 206; *A.*, 651.

[59] See also *Ann. Reports*, 1932, 271.

[60] *Bull. Soc. Chim. biol.*, 1932, **14**, 1235; *A.*, 106.

The importance of calcium as a nutrient for fungi, as distinct from the use of calcium carbonate as a neutralising agent in media, is further confirmed by A. Rippel and U. Stoess.[63] In *A. niger* and certain other cases, the calcium concentration of the medium exerts a marked effect on the growth of the mould only when abnormally large proportions of magnesium are present. It then appears to act as a regulator of intake (ion antagonism) and of the physiological functions. Similar effects are produced by partial substitution of strontium (as in the case of *Azotobacter* cited above) or tannin for calcium.

The action of fungi on arsenic compounds is apparently more common than is generally supposed. C. Thom and K. B. Raper [64] have isolated a number of organisms from soil. These produce arsenical gases when grown in arsenic-containing media, and several strains of *Penicillia* grow well on such media without producing gas. In the case of *P. brevicaule*, reported by F. Challenger,[65] trimethylarsine is formed from arsenites and from organic arsenical compounds, and quinquevalent arsenic compounds are reduced to tervalent.

Organic Acids and Other Products of Fungal Metabolism.—The production of formic acid by a number of species of *Aspergillus* and *Penicillium* is examined by T. Chrzaszcz and M. Zakomorny.[66] The complete chain of transformations from sugar would appear to be: sugar ⟶ acetic ⟶ fumaric ⟶ glyoxylic ⟶ formic acid. With favourable growth conditions, formic acid accumulates before undergoing further decomposition to carbon dioxide and hydrogen. Under less favourable conditions formic acid may be converted into oxalic acid. The conversion of sodium and calcium formates into the corresponding oxalates and carbon dioxide is also recorded by K. Bernhauer and F. Slanina.[67] It is not quite clear from a consideration of the above papers whether oxalic acid is a necessary product of oxidation of formic acid or whether it appears as the result of a side reaction.

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[61] N. Porges, *Bot. Gaz.*, 1932, **94**, 197; *A.*, 188.

[62] N. Nielson and V. Hartelius, *Compt. rend. Trav. Lab. Carlsberg*, 1932, **19**, No. 8; *A.*, 1932, 661; *Biochem. Z.*, 1933, **259**, 340; **261**, 70; *A.*, 638, 751.

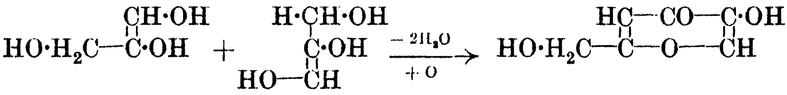
[63] *Arch. Mikrobiol.*, 1932, **3**, 492; *A.*, 97.

[64] *Science*, 1932, **76**, 549; *A.*, 189.

[65] *Ind. Chem.*, 1933, **9**, 134; *A.*, 638.

[66] *Biochem. Z.*, 1933, **259**, 156; **263**, 105; *A.*, 536, 982.

Various species of *Aspergillus* which produce kojic acid from sugars, inulin, etc., are examined by K. Sakaguchi.[68] Acid conditions and a suitable source of nitrogen favour the production of this acid,[68, 69] which is also stimulated by the presence of small amounts of iron, on a glucose substrate,[70] and by ethylene chlorohydrin.[71] A. J. Kluyver and L. H. C. Perquin [72] indicate that kojic acid is a direct product of transformation from glucose, but when it is obtained from fructose, galactose, xylose, arabinose, mannitol, erythritol, or glycerol, a C_6-carbohydrate is probably a necessary intermediate product. On the other hand Sakaguchi (*loc. cit.*), who obtained kojic acid from 3C-compounds and in one instance from ethyl alcohol, favours the conception that glucose is first broken down to 3-carbon compounds, which by oxidative condensation form the pyrone ring. This is in conformity with the original view of Corbellini and Gregorini,[73] who assumed the intermediate production of glyceraldehyde, thus,



$$\mathrm{HO{\cdot}H_2C{-}}\begin{array}{c}\mathrm{CH{\cdot}OH}\\ \|\\ \mathrm{C{\cdot}OH}\end{array} + \begin{array}{c}\mathrm{H{\cdot}CH{\cdot}OH}\\ |\\ \mathrm{C{\cdot}OH}\\ \|\\ \mathrm{HO{-}CH}\end{array} \xrightarrow[+O]{-2H_2O} \mathrm{HO{\cdot}H_2C{-}}\begin{array}{ccccc}\mathrm{HC} & - & \mathrm{CO} & - & \mathrm{C{\cdot}OH}\\ \| & & & & \|\\ \mathrm{C} & - & \mathrm{O} & - & \mathrm{CH}\end{array}$$

Kojic acid.

and receives further support from the formation of kojic acid from dihydroxyacetone by *A. Oryzæ* reported by H. Katagiri and K. Kitahara [74] (compare bacterial production of kojic acid, p. 310).

In a further series of papers H. Raistrick and his co-workers report considerable extensions of their already very comprehensive examination of the metabolic products of moulds. From media in which have grown *Penicillium brevi-compactum* and related species there have been isolated two mycophenolic acids

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[67] *Biochem. Z.*, 1933, **264**, 109; *A.*, 1082.

[68] *J. Agric. Chem. Soc. Japan*, 1932, **8**, 264; *A.*, 637.

[69] K. Katagiri and K. Kitahara, *Mem. Coll. Agric. Kyoto*, 1933, No. 26, 1; *A.*, 638.

[70] A. di Capua, *Gazzetta*, 1933, **63**, 296; *A.*, 983.

[71] O. E. May, G. E. Ward, and H. T. Herric, *Zentr. Bakt. Par.*, 1932, **86**, II, 129; *A.*, 1932, 1168.

[72] *Biochem. Z.*, 1933, **266**, 82; *A.*, 1332.

[73] *Gazzetta*, 1930, **60**, 244; *A.*, 1930, 959.

[74] *Mem. Coll. Agric. Kyoto*, 1933, No. 26, 1; *A.*, 638.

($C_{17}H_{20}O_6$),[75, 77] 3 : 5-dihydroxyphthalic acid,[75, 76] 3 : 5-dihydroxy-2-carboxybenzyl methyl ketone, 3 : 5-dihydroxy-2-carboxyphenylacetylcarbinol, and a hydrated form of 3 : 5-dihydroxy-2-carboxybenzoyl methyl ketone.[77] Luteic acid, previously reported as produced by *P. luteum* grown on glucose media, has now been obtained from a number of other sugars, glycerol, and succinic and citric acids when used as sole sources of carbon for the organism.[78] On a glucose–sodium nitrate medium, *P. griseo-fulvum* produces 2-hydroxy-6-methylbenzoic acid, mannitol, fumaric acid, and the newly recognised product, gentisic acid (2 : 5-dihydroxybenzoic acid).[79]

In an examination of *Helminthosporium gramineum*, the organism responsible for stripe disease in barley, there have been isolated from the mycelium helminthosporin (4 : 5 : 8-trihydroxy-2-methylanthraquinone) and hydroxy*iso*helminthosporin (probably 1 : 8-dihydroxy-2-hydroxymethylanthraquinone).[80] A related substance, cynodontin (probably 1 : 4 : 5 : 8-tetrahydroxy-2-methylanthraquinone), occurs in the mycelium of *H. cynodontis* and *H. euchlœnæ.*[81]

Biochemistry of the Higher Plants.

Mineral Nutrition.—The multiplicity of factors influencing the rate at which nutrients pass from the external medium into plant roots continues to be emphasised. Many workers have attempted to discover direct relationships between the concentration of individual ions in the nutrient and the rate of entry into the plant. For very dilute solutions a straight-line relationship may possibly exist, but under conditions obtaining in soils and still more in water culture experiments the mutual effects of solute ions both within and without the plant root become operative. Further, the assimilative and metabolic processes within the plant exert a powerful, if indirect, influence over the mechanism of intake by the roots. Thus S. A. Paxinos [82] shows that with dilute solutions of individual nutrients the intake curves were of very similar form to the dry matter production curves in point of view of both gradient and time distribution. When all nutrients were supplied simultaneously in a necessarily more

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[75] P. W. Clutterbuck, A. E. Oxford, H. Raistrick, and G. Smith, *Biochem. J.*, 1932, **26**, 1441; *A.*, 1932, 1289.

[76] A. E. Oxford and H. Raistrick, *ibid.*, p. 1907; *A.*, 189.

[77] A. E. Oxford, H. Raistrick, and P. W. Clutterbuck, *ibid.*, 1933, **27**, 634, 654; *A.*, 949.

[78] J. H. Birkinshaw and H. Raistrick, *ibid.*, p. 370; *A.*, 752.

[79] H. Raistrick and P. Simonart, *ibid.*, p. 628; *A.*, 949.

[80] J. H. V. Charles, H. Raistrick, R. Robinson, and A. R. Todd, *ibid.*, p. 499; *A.*, 752.

[81] H. Raistrick, R. Robinson, and A. R. Todd, *ibid.*, p. 1170; *A.*, 1082.

[82] *Z. Pflanz. Düng.*, 1933, **28**, [*A*], 1; *B.*, 402.

concentrated solution, nitrogen, phosphorus, and potassium entered the roots at rates which were relatively in advance of the dry matter production curves. The intake of magnesium and calcium lagged behind the increasing dry matter yields. An interesting exception to the general nature of base intake appears in the case of sodium, which penetrated at a very much enhanced rate from the more concentrated mixed nutrient. In experiments with a somewhat similar object G. Pfützer [83] shows further confirmation of the lack of direct relationship between nutrient concentration and intake except over small ranges of concentration. Working with tomato plants in soils of different moisture content, E. M. Emmert and F. K. Ball [84] also illustrate the different extents to which the intake of individual nutrients is affected by changing levels of water supply. Where moisture contents were low, the nitrate intake was not depressed, but that of phosphate declined considerably. This effect, combined with the depressive action of a lowered water supply on the general metabolism of plants, resulted in a high nitrate accumulation within the plant tissues. In an examination of the potash nutrition of plants D. R. Hoagland and J. C. Martin[85] indicate a general proportionality between the intake of potassium by crops and the potassium concentration of the soil solution in any one soil, *i.e.*, under conditions in which the proportional effect of other solutes would be generally similar. The relationship does not, however, apply to soils of different type in which the proportions of other ions would differ very considerably and also would be affected to different relative extents by natural changes in the water content of the soils. That the intakes of water and of dissolved ions are independent processes is shown by experiments of M. Gračanin.[86] Moreover the rate of water intake would appear to be approximately inversely proportional to the concentration of dissolved salts.[87]

Assimilation and Utilisation of Nitrogen.—There has been no abatement of interest during the year under review in the problem of the relative effects of the intake of nitrogen as nitrate and as ammonia.[88] A series of papers by J. W. Shive and his co-workers affords good illustration of the fact that the growth stage of the plant is an important factor influencing the utilisation of these two forms of nitrogen. Thus in the case of oats,[89] the young plants grew equally well in nutrients containing high concentrations of nitrate or of ammonia, but at a later stage the nitrate produced the more rapid growth. The ammonia and nitrate contents of the plants in the respective cases varied with the concentrations in the media. Plants supplied with nutrients in which the ratio $NH_4^{\bullet} : NO_3'$ was high had relatively higher proportions of soluble organic- and total organic-nitrogen and lower amounts of inorganic-nitrogen, than was the case when nitrates predominated in the nutrient. In another communication[90] the effects of supplying approximately equal proportions of ammonia and nitrate are recorded. Under these conditions also the intake of ammonia reaches a maximum in the early stages and that of nitrate at the flowering stage of the plants. The maximum rate of absorption of ammonia is much higher than that of nitrate. The total nitrogen intake curve therefore shows two maxima, the earlier being mainly dependent on ammonia intake and the later on that of nitrate. Throughout the growth period there is no actual cessation of absorption of either form of nitrogen. Very similar conditions prevail in the case of buckwheat,[91] except that the ammonia maximum is not attained until the beginning of flowering and that of nitrate after the flowering stage. Ammonia absorption is much more marked in buckwheat than in oats, the maximum rate of absorption of ammonia exceeding that of nitrate by about 600%.

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[83] *Landw. Jahrb.*, 1932, **76**, 745; *B.*, 403.

[84] *Soil Sci.*, 1933, **35**, 295; *B.*, 483.

[85] *Ibid.*, 1933, **36**, 1; *B.*, 804.

[86] *Compt. rend.*, 1932, **195**, 899; *A.*, 101.

[87] P. Mazé, P. J. Mazé, jun., and R. Axionnaz, *Compt. rend. Soc. Biol.*, 1933, **112**, 852; *B.*, 1027.

[88] Compare *Ann. Reports*, 1932, 255.

[89] A. C. Sessions and J. W. Shive, *Soil Sci.*, 1933, **35**, 355; *B.*, 564.

Differences both in dry matter production and in the distribution of nitrogen in cotton plants result from the use of nitrate and ammonia as nitrogen sources.[92] The former induced the heavier crop production, but when concentrated media were used the total nitrogen content of the "ammonia-plants" was the higher. With dilute solutions there was little difference between the total nitrogen contents in the two series of plants, but significant differences in the accumulation of nitrogen in roots, stems, and leaves indicated considerable differences in metabolic rates. H. C. M. Jacobson and T. R. Swanback[93] record an alternating dominance of intake of ammonia and of nitrate by tobacco similar to that which is recorded above for oats and buckwheat, from nutrients containing both forms of nitrogen. During hot seasons the plants wilted more readily as the proportion of ammonia in the nutrient increased. In cases in which ammonia formed the sole source of nitrogen, plants were stunted, were very susceptible to root rot infection, and contained abnormally low proportions of calcium. Ammonia toxicity towards tobacco is shown by experiments of A. B. Beaumont[94] to become apparent in media containing more than 6 p.p.m. of nitrogen in this form, and to be reduced by additions of sodium nitrate; the effect increases with the amount of nitrate supplied. In the early stages of growth, injury by ammonia may also be reduced by additions of calcium carbonate, but with increasing age the effect of the ammonium ion again predominates and the dry matter yield is adversely affected. It is concluded that ammonia toxicity is due to disturbed metabolism rather than to its physiologically acidic action. In sand-cultured apple trees rapid ammonia intake is associated with a lower reductase activity and also with a higher hemicellulose content than when normal proportions of nitrate are being assimilated.[95] The effect of light conditions on nitrogen assimilation is examined by L. S. Lubarskaja,[96] whose experiments show that the reduced utilisation of nitrogen by sugar beet seedlings in darkness is much more marked in the case of ammonia than of nitrates. Also the intake and utilisation of ammonium nitrate resembles more closely that of other ammonium salts than that of potassium nitrate.

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[90] A. L. Stahl and J. W. Shive, *Soil Sci.*, 1933, **35**, 375; *B.*, 564.

[91] *Idem, ibid.*, p. 469; *B.*, 727.

[92] K. T. Holley, T. A. Pickett, and T. G. Dulin, *Georgia Agric. Exp. Sta. Bull.*, 1931, No. 169; *B.*, 36.

[93] *Plant Physiol.*, 1933, **8**, 340; *B.*, 645.

The biological process of detoxication of ammonia within the plant system is examined and brought into close relationship with the p_H of the sap by M. Kultzscher.[97] The "ammonium plants" of Ruhland and Wetzel are those with highly acid saps in which ammonia is neutralised directly by organic acids and stored largely in the form of ammonium salts. In such plants deamination and deamidation is marked. Saps having $p_H > 5{\cdot}0$ are associated with "amide plants" in which ammonia is largely converted into the storage form of amide. The "mixed type" consists of plants of intermediate ranges of p_H associated with varying proportions of ammonia and amide in the stored nitrogen. No direct correlation between p_H and the NH_3 : amide ratio is apparent, and it must be concluded that factors other than sap reaction are operative in deciding the form of storage of nitrogen prior to elaboration into proteins.

A number of recent investigations are concerned with the effect of external conditions on the nitrogen metabolism of plants and the closely related process of carbon assimilation. In one of these, G. T. Nightingale[98] records the effects of temporary (10 day) changes of temperature on the metabolism of tomato plants. At the lower temperature examined (13°), although nitrate absorption and translocation took place freely, the reductase activity of the plants was low and protein synthesis retarded. Simultaneously there was considerable accumulation of carbohydrates, notably starch, leaves were deficient in chlorophyll, and stems showed anthocyanin coloration. In the absence of external supplies of nitrogen these conditions were intensified. Increase of temperature to 21° permitted greater utilisation of carbohydrates and synthesis of protein even in plants receiving no additional nitrogen. With external supplies of nitrate both processes were still more accelerated. Assimilation, translocation, and reduction of nitrate were much more rapid than at 13°. At a still higher temperature (35°) carbohydrate decomposition became extremely rapid and was associated with protein degradation even where external supplies of nitrate were available. Exhaustion of the plants soon occurred and was accelerated in those having access to nitrate supplies.

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[94] *Proc. 2nd Internat. Cong. Soil Sci.*, 1932, **4**, 65; *B.*, 85.

[95] V. A. Tiedjens and M. A. Blake, *New Jersey Agric. Exp. Sta. Bull.*, 1932, No. 547; *B.*, 981.

[96] *Z. Pflanz. Düng.*, 1933, [*A*], **28**, 340; *A.*, 647.

[97] *Planta* [*Z. wiss. Biol.*], 1932, **17**, 699; *A.*, 197.

[98] *Bot. Gaz.*, 1933, **95**, 35; *A.*, 1215.

The effect of varied rates of carbohydrate and nitrogen metabolism on fruit production in tomatoes is considerable. By controlling carbon assimilation through altered exposure to light and simultaneously varying the nitrogen supply, V. M. Watts[99] demonstrates that conditions producing an appropriate balance of carbohydrate and amino-acids within the plant system are necessary to ensure optimum fruiting. Thus excessive exposure to light, with its accompanying rise in carbohydrate formation, induces an increased dry matter production but lowers the nitrogen content of the plant and especially the amino-acid fraction: fruitfulness declines and a weak woody growth of stems takes place. At the other extreme, in which the nitrogen supply is maintained at a high level, but exposure to light is restricted, the ratio of amino-acid to carbohydrate tends to become unduly high, and unfruitful plants showing a very succulent form of growth are produced.

Differences in the level of nitrogen metabolism in highly manured apple trees are manifest in differences in the lipin- and residual-nitrogen fractions in the leaves. Corresponding changes in carbohydrate metabolism are characterised by the nature of the reserve (insoluble) matter.[1]

Potassium and Plant Growth.—The influence of the level of potash supply to plants on their water economy is emphasised in several recent publications. Deficiency of potassium tends to lower the total dry matter production of many plants but at the same time to reduce, to a greater extent, the water content of the tissues. This is ascribed by K. Schmalfuss[2] to the effect of potassium in modifying the colloidal nature of protoplasmic constituents, and thus exerting a partial control over the proportions of "free" and "bound" water in the tissues. The practical result of this action is shown by the increased drought resistance of plants receiving adequate supplies of potassium.[3, 4]

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[99] *Arkansas Agric. Exp. Sta. Bull.*, 1931, No. 267; *B.*, 1931, 243.

[1] N. W. Stuart, *New Hampshire Agric. Exp. Sta. Tech. Bull.*, 1932, No. 50; *A.*, 102.

Although it is generally recognised that a large proportion of the potassium content of plants remains in a soluble condition, it would appear that considerable amounts have undergone elaboration into complex compounds. Electrodialysis reveals that 35% of the total potash of young pea plants, and only 14% of that in older plants, migrates to the cathode, and 16% and 18% respectively appear at the anode, these proportions being independent of the nature of the membrane used. In discussing these results S. L. Inosemzev[5] indicates that the dialysable fraction of the potassium contains considerable amounts in organic combination. In recording the influence of the supply of potassium on the carbon assimilation of the leaves of cereals G. Gassner and G. Goetze[6] draw attention to the fact that in curves relating potash supply with assimilation (rising with increasing potassium concentration to a maximum point and subsequently declining), the maxima are different and characteristic for each cereal examined.

Intake and Utilisation of Phosphorus by Plants.—In addition to the known assimilation of inorganic phosphates by plants, many workers have obtained indications that a variety of organic phosphorus compounds of varying complexity may also be utilised. Recent work of J. Weissflog and H. Mengdehl[7] adds definition to this conception. Various types of phosphorus compounds are examined, and, according to their effects on maize plants, classified into three principle groups: (1) phytin group, which includes phytic and nucleic acids; (2) ortho-group, comprising phosphoric acid, hexose diphosphate, etc.; and (3) ester group, which includes hexose monophosphates, glyceryl and sucrose phosphates. Group (2) was the most effective as a source of phosphorus, as judged by the gross weight of the crop and its phosphorus content: (1) and (3) produced similar dry matter yields, but the percentage of phosphorus in the plants was greater with (3) than with (1). The order of efficiency of the organic substance was approximately that of the susceptibility to decomposition by the phosphatase of the maize. Plants utilising the ortho-group contained the greatest proportions of orthophosphates. Inferior utilisation of phytic and nucleic acids was indicated by accumulations of soluble organic and insoluble phosphorus in the plant roots. Among the inorganic compounds examined, pyro- and meta-phosphates were absorbed but were converted into ortho-phosphates before leaving the root systems. Hypophosphites and phosphites, although passing freely into the plant system, were not utilised.

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[2] *Phytopath Z.*, 1932, **5**, 207; *A.*, 545; *Z. Pflanz. Düng.*, 1933, **28**, [*A*], 330; *A.*, 649.

[3] M. A. H. Tincker and F. V. Darbishire, *Ann. Bot.*, 1933, **47**, 27; *A.*, 436.

[4] O. Tornau and K. Meyer, *J. Landw.*, 1933, **81**, 175; *B.*, 680.

[5] *Ergebn. Veg. Lab.-arb. Prianischnikov*, 1930, **15**, 85; *A.*, 650.

[6] *Planta* [*Z. wiss. Biol.*], 1933, **20**, 391; *B.*, 1026.

[7] *Ibid.*, 1933, **19**, 182, 242; *A.*, 648.

The nature of the phosphorus compounds in plants has been examined by a variety of methods. Earlier work frequently led to confusing results, since the methods of isolation often involved decomposition of the substances in question. To overcome this difficulty H. Magistris has examined the separation of organic phosphorus compounds by dialysis, and the effects of various salts on the process.[8] The general association of seed formation with phytin synthesis in plants is reflected in the number of records of investigation of the phosphorus distribution of seeds. In horse beans[9] and in hemp seed[10] the proportions of organic and inorganic phosphorus extractable with dilute acids and alkalis indicate the presence of phytic, nucleic, and inorganic phosphorus in the seed. In sunflower seed more than three quarters of the total phosphorus exists as phytin.[11] The phytin–lipin–nucleic- and inorganic phosphorus of wheat grain is examined by T. S. Andrews[12] and of the whole plant in various stages of growth by F. Knowles and J. E. Watkin.[13] The latter show that during the four months prior to harvesting the gross weight of lipin-phosphorus in the stems rose steadily until ear emergence and subsequently declined to a fairly constant value. In the ear the lipin weight was small and remained at a steady figure until shortly before harvesting. There was a steady transference of phytin and inorganic phosphorus from straw to ear as the grain matured. A close parallelism existed between variations of the phytin-phosphorus and protein-nitrogen throughout the period examined. In maize[14] phytin is absent from all parts of the plant until after pollination, and then appears only in the seed. During germination phytin disappears from the seed at an early date. Little variation occurs in the percentage of lipin- and acid (0·2% HCl)-insoluble organic phosphorus during growth of the plant. Translocation of phosphorus within the plant took place only with inorganic and acid-insoluble organic fractions.

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[8] *Biochem. Z.*, 1932, **253**, 64, 81; *A.*, 1932, 1181, 1203.

[9] E. Mnich, *Bull. Acad. Polonaise*, 1931, [*B*], 123; *A.*, 1932, 1181.

[10] E. Pischinger, *ibid.*, 1932, [*B*], 37; *A.*, 874.

[11] A. Goldovski and A. Bozhenko, *Masloboino Zhir. Delo*, 1932, No. 7, 30; *A.*, 1092.

[12] *Ind. Eng. Chem.*, 1932, **24**, 80; *B.*, 1932, 574.

[13] *J. Agric. Sci.*, 1932, **22**, 755; *A.*, 101.

[14] E. E. de Turk, J. R. Holbert, and B. W. Howk, *J. Agric. Res.*, 1933, **46**, 121; *A.*, 545.

Mineral Nutrition and the Incidence of Disease in Plants.—A very definitely increasing interest is being shown in this aspect of plant pathology. Economic pressure has stimulated enquiry into the quantitative as well as qualitative aspects of manurial problems and brought in its train numerous incidental observations of the health condition of plants in relation to nutrition. Also the continuously increasing outlay in curative measures has turned attention much more emphatically to the possibility of minimising crop injury by the often less costly method of adjusting nutrient conditions.

For many years the use of potash fertilisers has been recognised as a satisfactory method of reducing the susceptibility of plants to certain diseases. It is becoming increasingly apparent that, whilst the influence of potassium in this respect is a very important one, much more may depend on the relative proportions in which various mineral nutrients are supplied to plants than on the specific preventive capacity of any one of them.

The effect of potassium in reducing injury by yellow rust in barley, drought spot in oats, leaf roll in potato,[15] rust in wheat,[16] stripe disease in potatoes,[17] and wilt and rust in cotton [18] is recorded this year. The effect of anions associated with potassium on its action in increasing disease resistance is shown by E. Lowig.[19] The infection of cereals by *Erisiphe graminis* is reduced to a greater extent by applications of potassium silicate than by the carbonate, chloride, or sulphate, although no difference in manurial action is apparent.

In a number of instances, the proportion of calcium relative to other nutrients, and also in its relation to the reaction of the medium, appears to be concerned in the degree of infection by fungal diseases together with other diseases falling under the general heading of "nutritional disorders." The "damping off" of soya bean seedlings appears to be influenced much more by calcium deficiency than by the reaction of the nutrient.[20] Calcium deficiency or an excessive MgO : CaO ratio is associated with severe attacks of root rot in tobacco,[21] with "sand-drown" in tobacco and maize,[22] and with leaf wrinkle in soya beans.[23] "Speck" disease in oats is primarily the outcome of manganese deficiency, but is accentuated by unbalanced ionic ratios in the nutrient, notably that of K : Ca.[24] Sulphur deficiency is the cause of, or at least a heavily contributing factor in, the tea "yellows" disease.[25] An interesting investigation of the effects of unbalanced proportions of the three principal fertilisers on the infection of tomato plants by *Fusarium lycopersici* is recorded by H. Ahmet.[26] The susceptibility of the plants varied with nutrient supplies in the decreasing order: potassium deficiency, low phosphate, excessive nitrogen, excessive phosphate, excessive potassium, low nitrogen. An interesting resumé of the effects of unbalanced nutrition, of the absence of individual nutrients, and of other growth conditions on the distribution of plant disease is given by F. Labrousse.[27]

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[15] L. Kratschmer, *Ernähr. Pflanze*, 1933, **29**, 264; *B.*, 981.

[16] W. Acker and F. Konig, *ibid.*, p. 101; *B.*, 518.

[17] Köstlin, *ibid.*, p. 48; *B.*, 439.

[18] V. H. Young, G. Janssen, and J. O. Ware, *Arkansas Agric. Exp. Sta. Bull.*, 1932, No. 272; *B.*, 201.

[19] *Ernähr. Pflanze*, 1933, **29**, 162; *B.*, 646.

ANIMAL BIOCHEMISTRY.

Carbohydrate Utilisation in Muscle and Yeast.

THE period under review has seen important developments in the elucidation of the chemical processes of carbohydrate utilisation in both muscle and yeast. A new scheme of fermentation formulated by the late G. Embden and his collaborators[28] has been accepted and developed by O. Meyerhof and his school, and shown to be equally applicable to the muscle and yeast processes.

It will be remembered that O. Meyerhof, K. Lohmann, and R. Meier,[29] in an important paper dealing with carbohydrate formation during the recovery process in the intact muscle of the frog, showed that, apart from lactic acid, only pyruvic acid out of a considerable number of substances investigated, produced a recovery synthesis of sugar with oxygen uptake. Later, E. Toeniessen and E. Brinkmann[30] demonstrated that pyruvic acid was rapidly removed when perfused through the musculature of a rabbit. E. M. Case and R. P. Cook[31] isolated pyruvic acid and methylglyoxal from frog and rabbit muscle and formed the opinion that both participated in some muscle process. The occurrence of pyruvic acid was further investigated by Case,[32] who found that it was not an intermediate in lactic acid formation, nor was it a product of the oxidation of the latter acid. The possible rôle of pyruvic acid was further emphasised by A. Hahn and W. Haarmann[33] when they found that thoroughly washed muscle (free from lactic dehydrogenase) readily produced pyruvic acid from fructosediphosphoric acid. Numerous well-known investigations by C. Neuberg and his collaborators have established the importance of pyruvic acid in many yeast and bacterial fermentation processes.

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[20] W. A. Albrecht and H. Jenny, *Bot. Gaz.*, 1932, **92**, 263; *B.*, 1932, 200.

[21] T. R. Swanback and H. G. M. Jacobson, *Science*, 1933, **77**, 169; *B.*, 440.

[22] A. Gehring, *Ernähr. Pflanze*, 1932, **28**, 101; *B.*, 1932, 569.

[23] E. W. Hopkins, *Plant. Physiol.*, 1933, **8**, 333; *B.*, 644.

[24] H. Lumdegardh, *Medd. Centralanst. Försösksr Jordbruks.*, 1931, No. 403; *B.*, 1027.

[25] H. H. Storey and R. Leach, *Nyassaland Dept. Agric. Bull.*, 1932, No. 3; *B.*, 245.

[26] *Phytopath. Z.*, 1933, **6**, 49; *B.*, 840.

[27] *Ann. Agron.*, 1932, **2**, 774; *A.*, 437.

[28] G. Embden, Deuticke, and Kraft, *Klin. Woch.*, 1933, **12**, 213.

[29] *Biochem. Z.*, 1925, **157**, 459; *A.*, 1925, i, 727.

It was shown by K. Lohmann[34] and by F. Lipmann and K. Lohmann[35] that, when muscle tissue is minced in the presence of fluoride and added glycogen or starch, only a part of the hexosephosphoric acid ester which accumulates is the true Harden–Young fructose-1 : 6-diphosphoric acid. A considerable part, and sometimes even the whole, is found to be present in the form of an ester of the same elementary composition but possessing a much greater resistance to acid hydrolysis. In fact Lohmann called it the "unhydrolysable" ester. The monophosphoric esters isolated by Robison, Neuberg, and Embden were converted into this resistant ester by taking up one equivalent of phosphate from muscle extracts containing fluoride.

Early in the year under review G. Embden and his colleagues[36] found that a constituent of the Lohmann "unhydrolysable" ester was glyceric acid-monophosphoric acid (phosphoglyceric acid). This acid was first encountered by R. Nilsson[37] in 1930 and isolated as the barium and strychnine salts during his studies of the enzymic breakdown of carbohydrate by yeast. At about the same time as Embden's discovery another constituent of the Lohmann ester was isolated in Meyerhof's laboratory.[38] This was *l*-α-glycerophosphoric acid. Thus it appeared that the Lohmann ester consisted of equimolar proportions of phosphoglyceric acid and glycerophosphoric acid :

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[30] *Z. physiol. Chem.*, 1930, **187**, 137; *A.*, 1930, 637.

[31] *Biochem. J.*, 1931, **25**, 1319; *A.*, 1931, 1184.

[32] *Ibid.*, 1932, **26**, 759; *A.*, 1932, 875.

[33] *Z. Biol.*, 1930, **90**, 231; *A.*, 1930, 1064; see also A. Hahn, *ibid.*, 1933, **94**, 97; *A.*, 1194.

[34] *Biochem. Z.*, 1930, **222**, 324; *A.*, 1930, 1210.

[35] *Ibid.*, p. 389; *A.*, 1930, 1210.

[36] *Loc. cit.*

[37] *Arkiv Kemi, Min., Geol.*, 1930, **10**, [*A*], No. 7; *A.*, 1930, 641.

[38] *Nature*, 1933, **132**, 337, 373; *A.*, 1074; O. Meyerhof and D. McEachern, *Biochem. Z.*, 1933, **260**, 417; *A.*, 742.

$$(HO)_2PO{\cdot}O{\cdot}CH_2{\cdot}CH(OH){\cdot}CO_2H+(HO)_2PO{\cdot}O{\cdot}CH_2{\cdot}CH(OH){\cdot}CH_2{\cdot}OH.$$

Embden and his colleagues showed that phosphoglyceric acid is transformed into pyruvic acid by minced muscle. Moreover, although lactic acid was not produced by the addition of either pyruvic acid alone or α-glycerophosphoric acid alone to muscle extracts free from carbohydrate, it was found that the simultaneous addition of phosphoglyceric acid and α-glycerophosphoric acid to muscle brought about an increased formation of lactic acid. Furthermore the addition of pyruvic acid and of α-glycerophosphoric acid together did lead to the production of lactic acid, the amount of the latter formed being equivalent to twice the pyruvic acid which had disappeared, thus :

$$CH_3{\cdot}CO{\cdot}CO_2H + CH_2(OH){\cdot}CH(OH){\cdot}CH_2{\cdot}O{\cdot}PO(OH)_2 \longrightarrow 2CH_3{\cdot}CH(OH){\cdot}CO_2H + H_3PO_4.$$

Further insight into the probable course of the breakdown of sugar in muscle is obtained from a study of the behaviour of triosephosphoric acid. H. O. L. Fischer and E. Baer [39] have recently synthesised glyceraldehyde-γ-phosphoric acid and the dextro-component of their racemic compound has been shown by C. V. Smythe and W. Gerischer [40] to undergo fermentation by yeast with an initial velocity at least as great as that of glucose of the same molar concentration. Moreover Embden has corroborated the formation of lactic acid on adding glyceraldehyde phosphoric acid to muscle tissue. O. Meyerhof and W. Kiessling [41] have shown that in muscle extracts one half (*i.e.*, one optical component of the racemic compound) is transformed into phosphoglyceric and glycerophosphoric acids. When sulphite, but no fluoride, is added to the muscle extract, pyruvic and glycerophosphoric acids are formed. Meyerhof [42] points out that glyceraldehyde-γ-phosphoric acid is the first synthetic ester to be converted into lactic acid as easily as and by the same path as the naturally occurring phosphoric acid esters.

Embden summarised his views regarding these anaërobic processes in a scheme which may be represented as shown. According to these views the formation of lactic acid in muscle is a true oxidation–reduction process in which the mutation of hexosediphosphoric acid is involved, the oxidised product being pyruvic acid and the reduced *l*-α-glycerophosphoric acid.

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[39] *Ber.*, 1932, **65**, [*B*], 337; *A.*, 1932, 364.

[40] *Biochem. Z.*, 1933, **260**, 414; *A.*, 750.

[41] *Ibid.*, **264**, 40; *A.*, 1080; *Naturwiss.*, 1933, 21, 223; *A.*, 528.

[42] *Loc. cit.*

These new ideas are equally applicable to the scheme of yeast fermentation. Thus C. Neuberg and M. Kobel[43] have shown that yeast and the lactic acid bacterium (*B. Delbrücki*) transform phosphoglyceric acid into pyruvic acid. When yeast is used, some acetaldehyde is also formed. As has already been mentioned, Nilsson[44] in 1930 isolated phosphoglyceric acid from dried yeast acting on hexosediphosphoric acid in the presence of glucose, acetaldehyde, and fluoride. Meyerhof and Kiessling[45] have shown that in yeast maceration juice containing fluoride, hexosediphosphoric acid is converted, as in muscle extract, into Lohmann's "unhydrolysable" ester, *i.e.*, to the equimolecular mixture of α-glycerophosphoric acid and phosphoglyceric acid. Glyceraldehyde-γ-phosphoric acid behaves in similar fashion. Phosphoglyceric acid in fresh yeast extract is converted into acetaldehyde, carbon dioxide, and phosphoric acid. The acetaldehyde is reduced to alcohol, not by reacting with glycerophosphoric acid, but presumably[46] with the triosephosphoric acid arising from the interaction of glucose and hexosediphosphoric acid. Phosphoglyceric acid is formed simultaneously, thus:

$$(HO)_2PO{\cdot}O{\cdot}CH_2{\cdot}CH(OH){\cdot}CHO + CH_3{\cdot}CHO + H_2O \longrightarrow (HO)_2PO{\cdot}O{\cdot}CH_2{\cdot}CH(OH){\cdot}CO_2H + CH_3{\cdot}CH_2{\cdot}OH.$$

Meyerhof states that, apart from the presence of carboxylase, this reaction provides the main difference between alcoholic fermentation and lactic acid formation in muscle, the difference lying essentially in the fate of the pyruvic acid. The latter in muscle extract is reduced to lactic acid by interaction with glycerophosphoric acid, whilst in yeast it is split (by carboxylase) into carbon dioxide and acetaldehyde, the latter then being reduced as already explained to alcohol. It should be noted that acetaldehyde can be replaced by other reducible systems, for example, methylene-blue. These observations can be summarised in a scheme similar to that already given for the muscle process. One may finally remark that sodium fluoride presumably inhibits in both the muscle and the yeast process the splitting of phosphoric acid from phosphoglyceric acid and the consequent formation of pyruvic acid. In muscle, iodoacetic acid inhibits the interaction of glycerophosphoric acid with pyruvic

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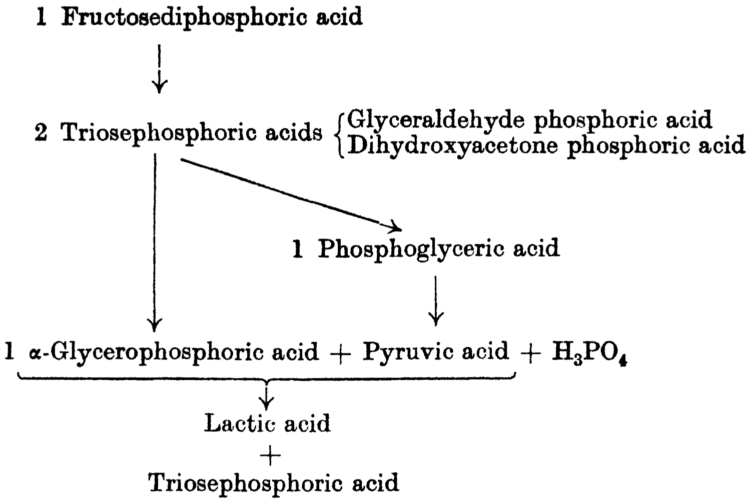
[43] *Biochem. Z.*, 1933, **260**, 241; *A.*, 637.

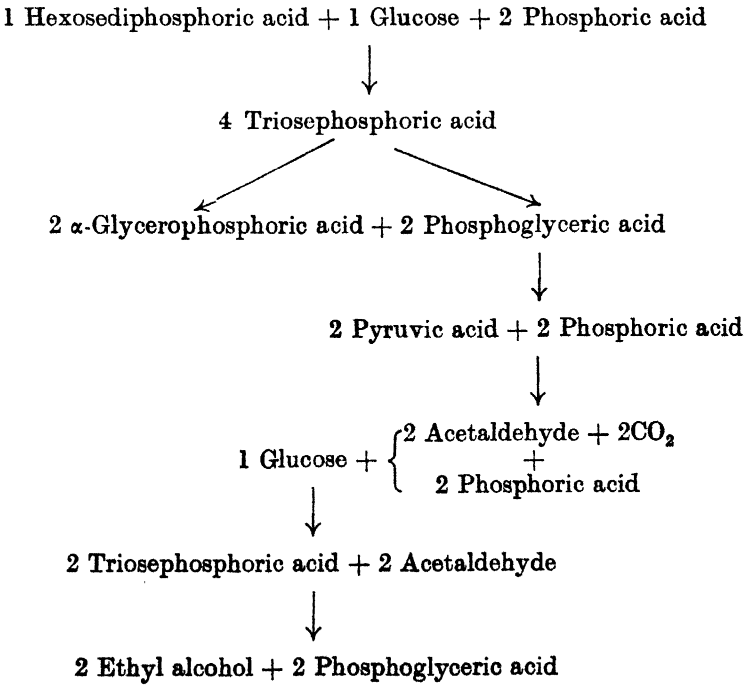
[44] *Loc. cit.*

[45] *Loc. cit.*

[46] See also F. Zuckerkandl and L. Messiner-Klebermass, *Biochem. Z.*, 1932, **255**, 330; *A.*, 188.


1 Fructosediphosphoric acid
2 Triosephosphoric acids
Glyceraldehyde phosphoric acid
Dihydroxyacetone phosphoric acid
1 Phosphoglyceric acid
1 α-Glycerophosphoric acid + Pyruvic acid + H_3PO_4
Lactic acid
+
Triosephosphoric acid

Representation of Embden's Fermentation Scheme.


1 Hexosediphosphoric acid + 1 Glucose + 2 Phosphoric acid
4 Triosephosphoric acid
2 α-Glycerophosphoric acid + 2 Phosphoglyceric acid
2 Pyruvic acid + 2 Phosphoric acid
1 Glucose +
2 Acetaldehyde + $2CO_2$
+
2 Phosphoric acid
2 Triosephosphoric acid + 2 Acetaldehyde
2 Ethyl alcohol + 2 Phosphoglyceric acid

Embden–Meyerhof Scheme of Yeast Fermentation.

acid and the consequent formation of lactic acid and triosephosphoric acid.

There can be no doubt that the developments just described represent a very considerable advance in our knowledge of carbohydrate utilisation, and they provide a welcome basis for the co-ordination of many previously isolated observations. The initiation of the new fermentation scheme is a fitting finale to the great services which Gustav Embden has rendered to biochemistry. Through his untimely death the science loses one of its most active and inspiring leaders.

Deaminisation.

H. A. Krebs has continued his work described last year[47] on the mechanisms of deaminisation. He finds[48] that the kidney is a site of this process no less important than the liver; indeed in the kidney of the rat deaminisation is more rapid than in the liver of the same animal. The ammonia formed by the kidney in this process is the source of the urinary ammonia, and the mechanism plays an important part in regulating the acid–base equilibrium. A number of optical antipodes of naturally occurring amino-acids (*e.g.*, *l*-alanine, *l*-valine, *d*-leucine, *d*-phenylalanine, and *d*-histidine) are deaminised by rat kidney some 10—20 times as rapidly as the naturally occurring forms. Perhaps the most interesting aspect of this part of Krebs' work is his direct experimental corroboration, using liver and kidney slices, of the Neubauer–Knoop theory of oxidative deaminisation with formation of the corresponding α-ketonic acid. In 1922 Y. Kotake[49] recorded the isolation of phenyl- and hydroxyphenylpyruvic acids from the urine of rabbits receiving large amounts of phenylalanine and tyrosine respectively, and N. F. Shambaugh, H. B. Lewis, and D. Tourtellotte[50] have more recently made closely similar observations. But apart from the phenylamino-acids, proof of the direct conversion into the keto-acids was lacking for the bulk of the amino-acids. In the present investigations Krebs records the practically quantitative conversions: alanine ⟶ pyruvic acid, α-aminobutyric acid ⟶ α-ketobutyric acid, phenylalanine ⟶ phenylpyruvic acid, valine ⟶ dimethylpyruvic acid, leucine ⟶ α-keto*iso*hexoic acid, *nor*leucine ⟶ α-keto-*n*-hexoic acid. The keto-acids have been isolated in each of the cases quoted. For the deaminisation oxygen is necessary and the process is shown to apply also to glycine, to dicarboxylic acids, and to diamino-acids.

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[47] *Ann. Reports*, 1932, **29**, 244.

[48] *Klin. Woch.*, 1932, **11**, 1744; *A.*, 1074; *Z. physiol. Chem.*, 1933, **217**, 191; *A.*, 856.

[49] *Ibid.*, 1922, **122**, 241; *A.*, 1922, i, 1218.

[50] *J. Biol. Chem.*, 1931, **92**, 499; *A.*, 1931, 1185.

In a further series of experiments, using dog, guinea-pig, and rabbit kidney slices, Krebs [51] describes the isolation of ketoglutaric acid from *d*-glutamic acid, and of oxalacetic acid (yielding pyruvic acid and carbon dioxide) from aspartic acid. In these cases it was necessary, in order to prevent further degradation of the α-ketonic acids, to treat the kidney slices with *M*/1000-arsenious acid.

H. Manderscheid [52] has investigated the process of urea formation in the livers of two of the lower vertebrates—*R. esculenta* and *T. græca.* There is revealed a mechanism similar to that of the mammalian liver, synthesis of urea being markedly accelerated by the addition of ornithine. It is concluded that when urea is formed in the vertebrates it is always by way of the ornithine ⟶ citrulline ⟶ arginine mechanism. Manderscheid has found that with the experimental methods used in these investigations, in birds and fish (the selachians are a possible exception),[53] there is no measurable synthesis of urea from ammonia and carbon dioxide. In birds the synthesis of uric acid is not influenced by ornithine.

Citrulline has now been isolated by M. Wada [54] from the products of tryptic digestion of caseinogen under conditions which do not lead to the conversion of arginine into citrulline. On the other hand F. Horn [55] records the formation of citrulline from arginine by *B. pyocyaneus* but not by *B. coli.* He postulates an arginine-desimidase distinct from arginase and trypsin.

Methionine.

During the past few years there have appeared several studies of the most recently discovered amino-acid methionine.[56] That this amino-acid probably plays an important rôle in metabolism is indicated by the fact that it is the principal sulphur-containing amino-acid of caseinogen and probably also of egg-albumin.[57] H. D. Baernstein,[58] who assumes that proteins contain no methoxyl compounds and no methylthiol compound other than methionine, gives methionine-sulphur contents varying from 26% of the total sulphur (in secalin) to 90% (in casein). It is probably justified, therefore, to regard methionine as quantitatively the most important sulphur-containing amino-acid in ordinary diet and in proteins other than sclero-proteins.

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[51] *Z. physiol. Chem.*, 1933, **218**, 157; *A.*, 976.

[52] *Biochem. Z.*, 1933, **263**, 245; *A.*, 976.

[53] See A. Hunter and J. A. Dauphinée, *Proc. Roy. Soc.*, 1924, [*B*], **97**, 227; *A.*, 1925, i, 104.

[54] *Proc. Imp. Acad. Tokyo*, 1932, **8**, 367; *A.*, 172.

[55] *Z. physiol. Chem.*, 1933, **216**, 244; *A.*, 753.

[56] *Ann. Reports*, 1928, **25**, 233; 1931, **28**, 234.

[57] N. W. Pirie, *Biochem. J.*, 1932, **26**, 2041; *A.*, 305.

[58] *J. Biol. Chem.*, 1932, **97**, 669; *A.*, 1932, 1149.

In 1924 J. H. Mueller,[59] the discoverer of methionine, showed that in man it was readily oxidised to sulphuric acid. N. W. Pirie [60] has recently extended these observations and finds that in the dog methionine is oxidised to the same extent as cystine. *S*-Ethylcysteine and *S*-benzylcysteine are not appreciably oxidised, whilst *S*-methylcysteine is oxidised but is too toxic to permit of accurate measurements. R. W. Jackson and R. J. Block [61] have shown that the addition of methionine to a diet deficient in cystine produces a marked increase in the weight of rats, and the same observers [62] state that equally effective growth responses are obtained in rats receiving *d*- or *l*-methionine or *l*-formylmethionine, whereas *d*-formylmethionine is devoid of action. Similar conclusions regarding the replaceability of cystine by methionine may be drawn from the results of A. White and H. B. Lewis,[63] who find that the increased urinary nitrogen elimination on a low cystine diet following the administration of bromobenzene is prevented by the addition of either *l*-cystine or *dl*-methionine. The further results of B. W. Chase and H. B. Lewis [64] show that in rats the absorption coefficient of *dl*-methionine from the gastro-intestinal tract is slightly greater than that of cystine. They also find that the urines of rats receiving methionine give the cyanide–nitroprusside test for the $-S-S-$ linking.

L. W. Butz and V. du Vigneaud [65] have recorded the formation of an interesting higher homologue of cystine by the decomposition of methionine with sulphuric acid. To this homocystine they ascribed the structure

$$HO_2C\cdot CH(NH_2)\cdot CH_2\cdot CH_2\cdot S\cdot S\cdot CH_2\cdot CH_2\cdot CH(NH_2)\cdot CO_2H$$

and this has been confirmed by V. du Vigneaud, H. M. Dyer, and J. Harmon [66] by the conversion of homocystine into homocysteine, by reduction with sodium in liquid ammonia, and subsequent methylation to yield methionine. The same workers confirm the growth-stimulating action of methionine on low cystine diets, but the main interest of their results lies in the finding that *dl*-homo-

[59] *J. Biol. Chem.*, 1924, **58**, 373; *A.*, 1924, i, 438.

[60] *Loc. cit.*

[61] *Science*, 1931, **74**, 414; *A.*, 1932, 83; *J. Biol. Chem.*, 1932, **98**, 465; *A.*, 89.

[62] *Proc. Soc. Exp. Biol. Med.*, 1933, **30**, 587; *A.*, 975.

[63] *J. Biol. Chem.*, 1932, **98**, 607; *A.*, 89.

[64] *Ibid.*, 1933, **101**, 735; *A.*, 1075.

[65] *Ibid.*, 1932, **99**, 135; *A.*, 151.

[66] *Ibid.*, 1933, **101**, 719; *A.*, 1074.

cystine likewise produces growth in rats in lieu of methionine or cystine. It may be that the action of homocystine is non-specific in simply supplying utilisable sulphur to the organism, but, as was shown by B. D. Westerman and W. C. Rose,[67] other disulphide acids, *e.g.*, dithiodiglycollic, β-dithiodipropionic, and α-dihydroxy-β-dithiodipropionic, are unable to support growth on cystine-deficient diets in spite of their oxidation in the body. The results of du Vigneaud and his colleagues are therefore in harmony with the view that demethylation may occur in the intermediary metabolism of methionine with subsequent formation of homocysteine.

Vitamin A.

The impetus which from time to time organic chemistry gains from biology has been demonstrated in several fields in recent years, but nowhere more strikingly than in the attempts to elucidate the structures of vitamins A and C and cognate problems. In previous years the relationship of vitamin A to natural polyene pigments of the carotene and related groups has been dealt with in this section of these Reports,[68] but the interest has now widened considerably and purely chemical problems of outstanding interest have arisen. Although these problems, and also those centring round the nature of vitamin C, may justly be regarded as biochemical in their inception, they are perhaps now more appropriately dealt with in the organic chemistry sections of these Reports. Thus the important and voluminous structural work of R. Kuhn and P. Karrer and their associates on the polyene group is described elsewhere in this volume.[69] The reader is referred to this account for details of the recent structural work on vitamin A and on carotene and related polyene pigments. It will be seen that the C_{22} formula tentatively advanced for the vitamin by Karrer in 1931 [70] still remains a possibility, although the $C_{20}H_{30}O$ structure is now preferred.[71] According to the latter, vitamin A is derived from exactly one half of the carotene molecule. The three α-, β-, and γ-carotenes so far described all possess growth-promoting action and it now appears that this action is dependent not on the number of double bonds present in the parent polyene hydrocarbon, but on the presence of at least one unmodified β-ionone ring.[72] T. Moore [73] has published data showing that β-carotene and a vitamin A concentrate are utilised equally efficiently by the rat when administered at levels approaching the minimum dose, and it is concluded that β-carotene possesses a biological activity equal to that of about the same weight of "pure" vitamin A. It would be interesting, as Moore suggests, to compare the activities of α- and γ-carotene with that of β-carotene at levels approaching the minimum dose. It is to be noted that, owing to the failure to secure crystalline preparations or derivatives of vitamin A, absolute criteria of its purity are still lacking. The preparation of F. H. Carr and W. Jewell [74] when administered to rats in daily doses of 0·006 mg. gave slightly better growth than 0·001 mg. (or 1 unit) per day of International Standard carotene. This would seem to be the purest preparation of vitamin A so far obtained.

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[67] *J. Biol. Chem.*, 1927, **75**, 533; 1928, **79**, 413, 423; *A.*, 1928, 87; 1928, 1396.

[68] *Ann. Reports*, 1929, **26**, 245; 1930, **27**, 276; 1931, **28**, 219; 1932, **29**, 248.

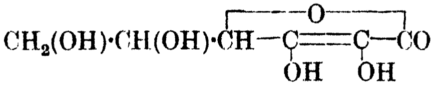
[69] P. 145.

[70] *Ann. Reports*, 1931, **28**, 221.

[71] P. Karrer, O. Walker, K. Schöpp, and R. Morf, *Nature*, 1933, **132**, 26; *A.*, 805; see also F. H. Carr and W. Jewell, *ibid.*, **131**, 92; *A.*, 323.

Vitamin C.

Last year an account was given of the progress made in the study of vitamin C and the steps which had led to a tentative identification of the vitamin with ascorbic acid.[75] Later work has all tended to confirm this identification, but the outstanding achievement in this field is the elucidation of the structure of ascorbic acid by E. L. Hirst and his collaborators,[76] and the synthesis of the *d*- and *l*-forms (the latter is the natural form) of this acid and of structurally analogous substances by W. N. Haworth, E. L. Hirst, and their collaborators [77] in the Birmingham laboratories. A detailed account of these brilliantly successful investigations is given elsewhere in these Reports.[78] It is sufficient to state here that the structure



$$\mathrm{CH_2(OH)\cdot CH(OH)\cdot \overbrace{CH-\underset{OH}{C}=\underset{OH}{C}-CO}^{O}}$$

deduced by Hirst and his co-workers from degradation and other experiments has been fully substantiated by the later syntheses.

Although it seems extremely probable that ascorbic acid is vitamin

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[72] R. Kuhn and H. Brockmann, *Naturwiss.*, 1933, **21**, 44; *A.*, 278; *Ber.*, 1933, **66**, [*B*], 407; *A.*, 431.

[73] *Biochem. J.*, 1933, **27**, 898; *A.*, 871.

[74] *Loc. cit.*

[75] *Ann. Reports*, 1932, **29**, 252.

[76] R. W. Herbert, E. L. Hirst, E. G. V. Percival, R. J. W. Reynolds, and F. Smith, *J.*, 1933, 1270; *A.*, 1143.

[77] R. G. Ault, D. K. Baird, H. C. Carrington, W. N. Haworth, R. Herbert, E. L. Hirst, E. G. V. Percival, F. Smith, and M. Stacey, *ibid.*, p. 1149; *A.*, 275.

[78] P. 167.

C, and numerous publications have appeared asserting or strongly suggesting that this is so,[79] it cannot yet be said that this is a certainty. It is clear, however, that the biological investigation of the synthetic material will place the matter beyond a doubt. At the time of writing data are not available.

J. L. Svirbely and A. Szent-Györgyi [80] find that the *iso*propylidene derivative of ascorbic acid [81] is a moderate antiscorbutic, whilst the acid recovered from it is fully active. E. L. Hirst and S. S. Zilva [82] have examined the vitamin C activity of various preparations of ascorbic acid, and although considerable variations in activity were noted,[83] it is found that active preparations can be regenerated from inactive, or much less active, oxidised preparations. A similar claim is made by V. Demole.[84] The general conclusion of Hirst and Zilva is that it is much more probable that ascorbic acid is active *per se*, than that the vitamin is associated with ascorbic acid and, like it, is reversibly oxidised and regenerated quantitatively. It is interesting to note that ascorbic acid immediately after oxidation with iodine shows little loss of antiscorbutic activity. This observation corroborates earlier statements of S. S. Zilva [85] and of J. Tillmans and his collaborators [86] as regards the vitamin present in decitrated lemon juice, and further confirmation is furnished by S. W. Johnson.[87] The explanation now favoured by Hirst and Zilva is that originally advanced by Tillmans, namely, that the vitamin itself, whilst retaining most of its activity, may be reversibly oxidised. It will be evident that the labile structure of ascorbic acid well fits it for such a rôle.

Vitamin B_1.

The identity of the various crystalline preparations [88] with which vitamin B_1 activity is associated is still uncertain. B. C. P. Jansen and his collaborators [89] now state that the analytical data agree best with the formula $C_{12}H_{18}O_2N_4S,2HCl$ for their air-dried vitamin hydrochloride.

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[79] See T. W. Birch, L. J. Harris, and S. N. Ray, *Nature*, 1933, **131**, 273; *A.*, 433; W. J. Dann, *ibid.*, p. 274; *A.*, 433; S. S. Zilva, *ibid.*, p. 363; *A.*, 433; A. L. Bacharach, *ibid.*, p. 364; *A.*, 433; L. J. Harris and S. N. Ray, *Biochem. J.*, 1933, **27**, 580; *A.*, 646.

[80] *Biochem. J.*, 1933, **27**, 279; *A.*, 541.

[81] *Ann. Reports*, 1933, **29**, 252.

[82] *Biochem. J.*, 1933, **27**, 1271; *A.*, 1091.

[83] Compare L. J. Harris and S. N. Ray, *loc. cit.*

[84] *Z. physiol. Chem.*, 1933, **217**, 83; *A.*, 756.

[85] *Biochem. J.*, 1927, **21**, 689; *A.*, 1927, 702.

[86] *Ann. Reports*, 1932, **29**, 252.

[87] *Biochem. J.*, 1933, **27**, 1287; *A.*, 1090.

[88] *Ann. Reports*, 1932, **29**, 250.

[89] B. C. P. Jansen, J. P. Wibaut, P. J. Hubers, and P. W. Wiardi, *Rec. trav. chim.*, 1933, **52**, 366; *A.*, 645.

During the past few years a series of investigations of the physiological action of vitamin B_1 has been in progress in the Oxford laboratories. These are of considerable interest in view of the new fermentation schemes of Embden and Meyerhof. There has frequently been discussed in the literature a supposed association between the antineuritic vitamin and certain aspects of carbohydrate metabolism, but it is only recently that the work of R. A. Peters and his co-workers has established a clear correlation. In 1929 H. W. Kinnersley and R. A. Peters [90] found that the brains of polyneuritic pigeons have a high lactic acid content, and Peters with N. Gavrilescu [91] showed a little later that the brain tissue from such pigeons has *in vitro* a sub-normal oxygen uptake. The latter workers then found,[92] on adding a concentrate of vitamin B_1 to the polyneuritic brain tissue *in vitro*, that the oxygen uptake was increased. The effect was obtained with the optic lobes and with lower parts of the brain and later with the cerebral and higher parts. So far no other tissue is known to show this effect.

N. Gavrilescu, A. P. Meiklejohn, R. Passmore, and R. A. Peters [93] established the specificity of the effect in the presence of added glucose or lactic acid. Experiments by A. P. Meiklejohn, R. Passmore, and R. A. Peters [94] on birds recovering from polyneuritis after treatment with vitamin B_1 concentrate, showed that there was an improvement in the oxidative behaviour towards lactate of minced brain from such birds, corresponding to the disappearance of the nervous symptoms, and with this improvement the effect of added vitamin B_1 concentrate *in vitro* diminished. It seemed, therefore, that vitamin B_1, or a substance present in B_1 concentrates, was capable of repairing the same defect both in the living bird and in the isolated brain.

The behaviour with regard to pyruvic acid, a question of obvious interest, differs from that shown towards lactic acid. Although the normal pigeon's brain when minced gives a large oxygen uptake, and the avitaminous brain a low oxygen uptake, both in the presence of pyruvic acid, the low uptake is not usually increased in this case by vitamin B_1 concentrates *in vitro*, although results are somewhat variable. The effect of vitamin B_1 seemed, therefore, to be related to lactic acid formation, with the possibility that pyruvic acid played some secondary rôle. E. Boyland [95] has shown that the vitamin is not a co-enzyme for lactic acid oxidation, and A. P. Meiklejohn [96] has obtained no evidence of an increased disappearance of lactic acid corresponding to the increased oxygen uptake.

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[90] *Biochem. J.*, 1929, **23**, 1126; 1930, **24**, 711; *A.*, 1929, 1496; 1930, 963.

[91] *Ibid.*, 1931, **25**, 1397; *A.*, 1931, 1338.

[92] *Ibid.*, p. 2150; *A.*, 1932, 200.

[93] *Proc. Roy. Soc.*, 1932, [*B*], **110**, 431; *A.*, 1932, 644; *Biochem. J.*, 1932, **26**, 1872; *A.*, 195.

[94] *Proc. Roy. Soc.*, 1932, [*B*], **111**, 391; *A.*, 1932, 1175.

R. A. Peters and H. M. Sinclair [97] have continued these studies and find that after previous washing of the avitaminous brain tissue its oxygen uptake under the influence of vitamin B_1 is reduced. The *in vitro* action of B_1 upon the avitaminous brain is abolished by cyanide and fluoride, whilst pyrophosphate interacts with B_1 and lactate to produce large rises in oxygen uptake over periods of from 2 to 3 hours. On the other hand, hexosediphosphate and Robison's monophosphate increase only the initial rate in avitaminous (as in normal) brains, but the effect is not sustained and there is no specific interaction with the vitamin. Of particular interest is the observation that α-glycerophosphate (but not the β-isomeride) increases the respiration largely, but the increase is not related directly to the specific vitamin action. Freshly minced avitaminous brain gives no pyruvate reaction, but this appears strongly after shaking with lactate–Ringer solution at p_H 7·3. It is suggested that pyruvate is formed from phosphoglycerate, which would account for the observed ready disappearance of the reaction in the presence of α-glycerophosphate. Although, therefore, there is no evidence at present to suggest that the vitamin action is concerned with α-glycerophosphate, or directly with pyruvate, it is inferred that α-glycerophosphate is probably one of the missing tissue substrates and that, since vitamin B_1, lactic acid, and pyrophosphate appear to form a coupled oxidation system, the vitamin lack must affect more than one phase of cellular metabolism.

Carcinogenesis by Pure Hydrocarbons.

In continuation of their work reported last year [98] J. W. Cook and his associates [99] have now isolated from a medium soft pitch an actively carcinogenic hydrocarbon in a state of purity. This is 1 : 2-benzpyrene. It was obtained along with the inactive 4 : 5-benzpyrene, 1 : 2-benzanthracene, and perylene. The structures of both benzpyrenes, and the physiological activity of the 1 : 2-isomeride, have been confirmed by synthesis. This new hydrocarbon is the most active carcinogenic substance now known and its isolation and synthesis constitute a remarkable advance in this field.

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[95] *Biochem. J.*, 1933, **27**, 786; *A.*, 872.

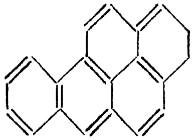
[96] *Ibid.*, p. 1310; *A.*, 1090.

[97] *Ibid.*, 1933, No. 6.

[98] *Ann. Reports*, 1932, **29**, 246.

[99] J. W. Cook, C. L. Hewett, and I. Hieger, *Nature*, 1932, **130**, 926; *A.*, 85; *J.*, 1933, 395; *A.*, 601.

Like the synthetic carcinogenic hydrocarbons previously described, 1 : 2-benzpyrene contains the 1 : 2-benzanthracene nucleus. It will be remembered that 1 : 2-benzanthracene is itself inactive, or very nearly so, but that it yields substances, sometimes of a very high order of carcinogenic activity, by the substitution of alkyl groups at position 6 or of new rings in the 5 : 6-position. J. W. Cook[1] makes the interesting statement that a mouse tumour produced by 1 : 2 : 5 : 6-dibenzanthracene has now reached the 67th transplanted generation, and in rats the 40th generation has been attained. Spindle-celled tumours, with metastases in the heart and other organs, have also been obtained by the injection of 1 : 2 : 5 : 6-dibenzanthracene into fowls.



1 : 2-Benzpyrene.

Synthetic Œstrogenic Substances.

It will be observed that the tricyclic phenanthrene ring system is common to all the carcinogenic hydrocarbons so far described. This system is now known to be present in a considerable number of naturally occurring substances of great physiological interest. Amongst these are the bile acids and sterols, vitamin D (calciferol), the ovarian hormones (œstriol and œstrone),[2] the cardiac-stimulating glucosides (strophanthin and digitoxin),[3] and certain alkaloids such as morphine and codeine of the opium group, and the corydalis alkaloids and colchicine. It is for this reason that the results of J. W. Cook, E. C. Dodds, and C. L. Hewett[4] are of great interest. These workers found that the synthetic substance 1-keto-1 : 2 : 3 : 4-tetrahydrophenanthrene could induce œstrous when injected into castrated animals, and Cook and Dodds[5] found that similar effects were obtained with 1 : 2 : 5 : 6-dibenz-9 : 10-di-*n*-butylanthraquinol and with the carcinogenic substances 5 : 6-*cyclo*penteno-1 : 2-benzanthracene and 1 : 2-benzpyrene. More detailed results have been presented by J. W. Cook, E. C. Dodds, C. L. Hewett, and W. Lawson,[6] who investigated a series of diols derived from 1 : 2 : 5 : 6-

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[1] Contribution to "Discussion on Experimental Production of Malignant Tumours," *Proc. Roy. Soc.*, 1933, [*B*], **113**, 275.

[2] This vol., p. 216.

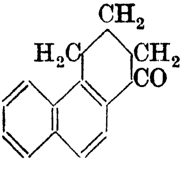
[3] W. A. Jacobs and E. E. Fleck, *J. Biol. Chem.*, 1932, **97**, 57; *A.*, 1932, 948; see also W. A. Jacobs and N. M. Bigelow, *ibid.*, 1933, **99**, 521; *A.*, 278.

[4] *Nature*, 1933, **131**, 56; *A.*, 323.

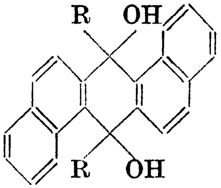
[5] *Ibid.*, p. 205; *A.*, 323.

[6] Communicated at the Meeting of the Royal Society, Nov. 16th, 1933.

dibenzanthracene. These have the general formula shown. Of these the dimethyl, di-*n*-amyl, and di-*n*-hexyl compounds are inactive, whilst the intermediate diethyl, di-*n*-propyl, and di-*n*-butyl compounds are all highly active, the propyl derivative showing the maximum activity. In addition to the compounds already mentioned, *neo*ergosterol, calciferol, and ergosterol also exhibit some œstrogenic action, diminishing in the order cited. The hydrocarbons are the least active of the œstrogenic substances so far investigated and it appears that the presence of oxygen-containing groups greatly increases the potency. In all cases the active substances contain the phenanthrene ring system. S. Aschheim and W. Hohlweg,[7] who record the presence of œstrogenic substances in extracts of bituminous materials, have no doubt encountered the same, or similar, hydrocarbons or derivatives of these. There is so far no evidence that carcinogenic substances are formed from œstrin in the animal body, but, none the less, B. P. Wiesner and A. Haddow [8] find that rats treated with naturally occurring œstrogenic hormone show, in contrast to non-treated rats, a marked increase in the rate of growth of implants of Jensen sarcoma.



1-Keto-1 : 2 : 3 : 4-tetrahydrophenanthrene



Diols related to 1 : 2 : 5 : 6-dibenzanthracene

The Œstrin Group.

In a praiseworthy attempt to systematise nomenclature in the œstrin group it has been suggested [9] that the follicular hormone hydrate (trihydroxyœstrin, theelol, emmenin) first characterised by Marrian should be designated "œstriol," and the follicular hormone (ketohydroxyœstrin, theelin) of Butenandt similarly designated "œstrone."

It is satisfactory to record results which place beyond doubt the relationship of members of the œstrin to the cholane group, for which assumed relationship much circumstantial evidence admittedly existed. A. Butenandt, H. A. Weidlich, and H. Thompson [10] have converted œstriol (hormone hydrate) by fusion with potassium hydroxide into a phenoldicarboxylic acid ($C_{18}H_{22}O_5$) formed by fission of the five-membered ring between the two secondary hydroxyl groups. Dehydrogenation of this dicarboxylic acid with selenium yielded hydroxy-1 : 2-dimethylphenanthrene, which was converted by distillation with zinc dust into 1 : 2-dimethylphenanthrene. The last-mentioned compound was also obtained by similar means from ætiobilianic acid of the cholane series.

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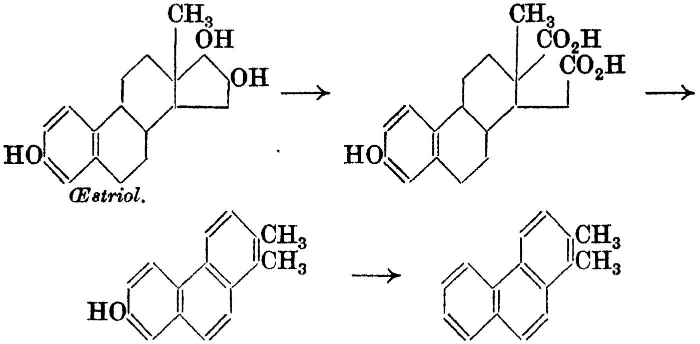
[7] *Deut. med. Woch.*, 1933, **59**, 12; *A.*, 870.

[8] *Nature*, 1933, **132**, 97; *A.*, 852.

[9] N. K. Adam, J. F. Danielli, E. C. Dodds, H. King, G. F. Marrian, A. S. Parkes, and O. Rosenheim, *ibid.*, p. 205.

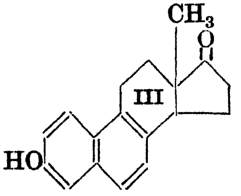
[10] *Ber.*, 1933, **66**, [*B*], 601; *A.*, 540.



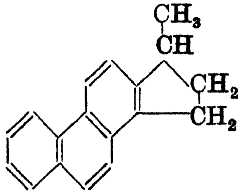
Œstriol.

1 : 2-*Dimethylphenanthrene.*

A. Girard, G. Sandulesco, A. Fridenson, and J. J. Rutgers,[11] continuing their investigations of the sex hormones of pregnant mare's urine,[12] have characterised equilenin[13] as $C_{18}H_{18}O_2$. This has a higher acidity than œstrone and apparently differs from it in having two aromatic rings in place of one. It would therefore have the constitution shown and it represents a natural dehydrogenation product of œstrone. It is of interest to note that the reduction of the keto- and hydroxyl groups and the aromatisation of ring III would yield a methyl*cyclo*pentenophenanthrene. Such a compound, $C_{18}H_{16}$, has been obtained from sterols and bile acids by O. Diels, W. Gädke, and P. Körding[14] by dehydrogenation with selenium. O. Rosenheim and H. King[15] suggested that this hydrocarbon was



Equilenin.



3-Methyl-1 : 2-*cyclo*pentenophenanthrene.

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[11] *Compt. rend.*, 1932, **195**, 981; *A.*, 98.

[12] *Ann. Reports*, 1932, **29**, 242.

[13] See *A.*, **1932**, **433**.

[14] *Annalen*, 1927, **459**, 1; *A.*, 1928, 169.

[15] *J. Soc. Chem. Ind.*, 1933, **52**, 299.

3-methyl-1 : 2-*cyclo*pentenophenanthrene and this has now been confirmed by its synthesis by G. A. R. Kon.[16] It is apparent, therefore, that a migration of the methyl group must occur during selenium dehydrogenation, and the earlier observation of Diels and Gädke[17] that more drastic dehydrogenation of cholesterol yielded the fully aromatic tetracyclic hydrocarbon chrysene, $C_{18}H_{12}$, must depend upon a further migration of carbon leading to ring enlargement. A. Butenandt[18] has recorded the formation of a hydrocarbon $C_{18}H_{14}$ by zinc dust distillation of œstrone. This may be impure chrysene.[19] The hydrocarbon $C_{17}H_{14}$, 1 : 2-*cyclo*pentenophenanthrene, has recently been synthesised by G. A. R. Kon[20] and independently by J. W. Cook and C. L. Hewett.[21] This is Diels's original hydrocarbon minus its methyl group. Thus remarkably interesting developments in the chemistry of the polycyclic hydrocarbons have rapidly followed the biological problems discussed in this and the preceding two sections of this Report.

Flavins or Lyochromes.

The important newly-discovered group of flavin dyes or lyochromes is described elsewhere in this volume.[22] The flavins are water-soluble, nitrogenous substances which have been isolated from human and canine liver and kidney (P. Ellinger and W. Koschara),[23] and from egg-white and milk whey (R. Kuhn and co-workers).[23] A flavin is also found associated with a protein in the new oxidation enzyme isolated from yeast juice (O. Warburg and W. Christian),[23] and the co-enzyme (cytoflav) of I. Banga and A. Szent-Györgyi[24] is stated by K. Laki[25] to be identical with the flavin component of the Warburg oxidation enzyme. The preparations obtained by Kuhn and his co-workers possess an intense vitamin B_2 activity, and a preparation of lactoflavin (from whey) is claimed to have the highest B_2 activity so far recorded. The flavins would seem to show every promise of a bright future.

A. G. Pollard.
J. Pryde.

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[16] *J. Soc. Chem. Ind.*, 1933, **52**, 950.

[17] *Ber.*, 1927, **60**, 140; *A.*, 1927, 241.

[18] *Nature*, 1932, **130**, 238; *A.*, 1932, 971.

[19] See *J. Soc. Chem. Ind.*, 1933, **52**, 268, 287.

[20] *J.*, 1933, 1081; *A.*, 1153.

[21] *Ibid.*, p. 1098; *A.*, 1299.

[22] P. 159.

[23] This vol., p. 159.

[24] *Biochem. Z.*, 1932, **246**, 203; **247**, 216; *A.*, 1932, 537, 775.

[25] *Ibid.*, 1933, **266**, 202; *A.*, 1318.

SUB-ATOMIC PHENOMENA AND RADIOACTIVITY.

THE eventful time in nuclear physics, characterised last year [1] by the discovery of the neutron and the hydrogen atom of mass 2, has continued. A particle, apparently the same in mass and charge as the electron but of opposite sign, has been observed for the first time, and is now easily produced in the laboratory. The "diplon" or "deuton," the nucleus of the hydrogen atom of mass 2, has proved itself a powerful projectile against the nuclei of light elements and is as promising a weapon as the proton. The artificial disintegration of light nuclei has now reached a stage where the proton, the diplon, the neutron, and the α-particle each have their merits as projectiles. After their temporary capture, any of these four, or, in addition, the positive electron, may emerge in the ensuing break-up. The number of isotopes found during the period under review is smaller than usual, but only because the elements still to be examined are very rare or difficult to study. Accurate determinations of atomic masses and isotopic abundances have been made. Interest in radioactivity, as formerly understood, has declined; the work done has been mainly among the rare-earth elements. The penetrating radiation which had latterly come to be described as "cosmic" has continued to be the subject of wide study and interpretation. There is no dispute about its penetration. The tendency, noted last year,[2] to replace "radiation" at least in part by "particle" continues; "cosmic," also, may conceivably be replaced by "terrestrial."

Radioactivity of Samarium.

G. von Hevesy and M. Pahl [3] have continued their work [1] on samarium. They find that 1 g. of the element emits 75 α-particles per second; the half-period is in consequence $1{\cdot}2 \times 10^{12}$ years. The particles have an initial velocity of $1{\cdot}05 \times 10^9$ cm. and a range approximately of 1·1 cm. at 15°. This success has stimulated investigations of the radioactivity of neighbouring rare-earth elements. M. Curie and S. Takvorian [4] have fractionated a mixture of neodymium and samarium oxides. In the fraction in which element 61 was to be expected, α-particles more penetrating than those from samarium were observed. These are possibly due to traces of element 61 at a concentration which has proved to be too small to be detected spectroscopically. Gadolinium[5] and lanthanum[3, 4] are definitely inactive, although the latter sometimes shows an activity which has been traced to actinium and its products.[3, 4] W. Yeh[6] confirmed the complete absence of activity in lanthanum but found with a Geiger–Müller counter a very feeble α-particle emission from neodymium. G. von Hevesy and M. Pahl[3] raised the question whether J. Joly's " hibernium " is not samarium. The latter[7] found in the pleochroic haloes in Archæan mica two very small rings which corresponded with ranges of α-particles in air at 15° of 1—1·2 and 2·1 cm. (Rings of similar radii were later found also by S. Iimori and J. Yoshimura.)[8] They must be due to traces of unknown radioactive elements and are the only rings that cannot be ascribed to known radio-elements. The element giving the smaller range and named " hibernium " may be samarium on account of the similarity of range. J. H. J. Poole[9] would agree with this if range were the only criterion; he calculated, however, that if the speck of material in the mica is samarium the number of α-particles it has expelled since its imprisonment is, in the happiest circumstances, only one-fifth of what is the minimum to give the rings J. Joly observed; to identify the two it would have to be shown that the " hibernium " mica was specially sensitive to marking by α-particles. No name has been given to the emitter of the particles of range 2·1 cm., nor has any identification of it with a supposed active element been made. It may be element 87[10] (which, on general grounds, is likely to expel α-particles) or element 61[4] or neodymium.[6] Further work on the radioactivity of these elements is necessary to test this view. If " hibernium " prove to be samarium, it can be calculated that the mica has acted as a detector of a radio-element which has expelled an average of only two α-particles per thousand years—surely a record in sensitivity.

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[1] *Ann. Reports*, 1932, **29**, 299.

[2] *Ibid.*, p. 313.

[3] *Nature*, 1933, **131**, 434; *A.*, 442; *Z. Physik*, 1933, **83**, 43; *A.*, 762.

[4] *Compt. rend.*, 1933, **196**, 923; *A.*, 442.

Isotopes and Mass-spectra.

During the year, knowledge of the isotopic composition of eight elements has been extended. The results are summarised in Table I.

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[5] W. F. Libby and W. M. Latimer, *J. Amer. Chem. Soc.*, 1933, **55**, 433; *A.*, 204.

[6] *Compt. rend.*, 1933, **197**, 142; *A.*, 882.

[7] *Proc. Roy. Soc.*, 1922, [*A*], **102**, 682; *Ann. Reports*, 1928, **25**, 316.

[8] *Ibid.*, p. 315.

[9] *Nature*, 1933, **131**, 654; *A.*, 551.

[10] *Ann. Reports*, 1932, **29**, 300.

TABLE I.

Element.	Atomic number.	Minimum number of isotopes.	Masses (nearest integer) of isotopes in order of abundance, except where parentheses are given.
Zinc	30	5	64, 66, 68, 67, 70
Cadmium ...	48	8	114, 112, 110, 111, 113, 116, (108, 118)
Tellurium ...	52	8	130, 128, 126, 125, 124, 122, 123, (127)
Neodymium	60	5	142, 144, 146, (143, 145)
Samarium ...	62	5	152, 154, (147, 148, 149)
Europium ...	63	2	151, 153
Gadolinium	64	5	(155, 156, 157, 158, 160)
Terbium	65	1	159

The work on zinc and tellurium [11] was done by K. T. Bainbridge. He found that the Zn^{65} and Zn^{69} ions measured by F. W. Aston [12] were quite certainly hydrides of Zn^{64} and Zn^{68}; the number of isotopes must therefore be reduced to five. F. W. Aston's order of relative abundance of these was confirmed. For tellurium, F. W. Aston's analysis [13] was confirmed and extended; Te^{124}, Te^{123}, Te^{122} with faint indications of Te^{127} were found. Te^{124} forms an isobaric triplet with the heaviest isotope of tin and the lightest of xenon. The atomic weights of zinc and tellurium calculated from these mass-spectrographic data, $65{\cdot}32 \pm 0{\cdot}02$ and $127{\cdot}58 \pm 0{\cdot}15$ respectively, are in excellent agreement with the International values. In an investigation of the isotope effect in the spectrum of cadmium hydride, E. Svensson [14] found components belonging to Cd^{118} and Cd^{108} in much smaller abundance than those already known; their abundances were not noticeably different. After a long and troublesome series of investigations, F. W. Aston [15] has now made a provisional analysis of some of the rare-earth elements. The results give at present only a rough estimate of relative abundance; the packing fractions have yet to be determined. Nd^{143} and Nd^{145} have been found in addition to the more abundant Nd^{142}, Nd^{144}, and Nd^{146}. Samarium gave a strong pair Sa^{152} and Sa^{154} and a weaker triplet Sa^{147}, Sa^{148}, Sa^{149}. Europium consists of Eu^{151} and Eu^{153} in roughly equal abundance, in agreement with the atomic weight 152·0. Gadolinium has five isotopes of undetermined abundance. Terbium is Tb^{159} only; there is certainly no Tb^{161} in the abundance which the atomic weight 159·2 suggests.

The isotopic composition of seventy of the ninety-two elements has now been investigated. Of the twenty-two which remain, numbers 43, 61, 84, 85, 86, 87, and 89 are very rare, numbers 88, 90, and 91 are less rare but radioactive, and six, numbers 66—71, are rare earths. It is intended to investigate the rare earths, masurium, thorium, and protoactinium in the near future. Protoactinium is the element whose atomic weight is most anxiously awaited. The determination [16] by chemical methods is still lacking. If the value should be 231, as simple theory suggests,[17] that point would be settled; if it should be 233, as has also been suggested,[17] material particles other than the α-particle must be expelled in the actinium series, and these might be found with the technique recently developed for detecting protons, diplons, and neutrons.

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[11] *Physical Rev.*, 1932, [ii], **39**, 847, 1021; *A.*, 1932, 1099.

[12] *Ann. Reports*, 1928, **25**, 306.

[13] *Ibid.*, 1926, **23**, 280; 1932, **29**, 303.

[14] *Nature*, 1933, **131**, 28; *A.*, 108.

[15] *Ibid.*, **132**, 930.

Twenty-two of the seventy elements investigated are simple, *i.e.*, have one mass only. In the range of mass-numbers 1—210, about one-fifth of them are still unappropriated by any element; thirty-one (twenty-four of even mass) are isobares of which three (two of even mass) are shared by a third element. These figures do not include the isobares 23 and 39, because the existence of Ne^{23} and Cl^{39}, although they still receive support on optical evidence,[18] is doubtful on mass-spectrographic evidence; they include 203 which is a possibility for lead as well as a certainty for thallium and mercury.

Exact knowledge of the masses of the isotopes of the light elements is becoming increasingly important in experimental work on artificial disintegration and for theories of nuclear structure. In Table II are given the isotopic masses determined (or redetermined with increased accuracy) since the last list [19] was given. (O^{16} = 16·0000, He^4 = 4·00216.)

TABLE II.

Atom.	Mass.	Atom.	Mass.	Atom.	Mass.	Atom.	Mass.
H^1	1·007775	O^{17}	17·0029	Se^{78}	77·937	Ba^{138}	137·916
H^2 or D	2·01363	O^{18}	18·0065	Se^{80}	79·941	Ta^{181}	180·927
Li^6	6·0145	Ne^{20}	19·9967	Nb^{93}	92·926	W^{184}	184·00
Li^7	7·0146	Ne^{22}	21·9947	Mo^{98}	97·945	Re^{187}	186·981
Be^9	9·0155	Si^{28}	27·9818	Mo^{100}	99·945	Os^{190}	189·981
B^{11}	11·0107	Cr^{52}	51·948	Te^{126}	125·937	Os^{192}	191·981
C^{13}	13·0039	Ni^{58}	57·942	Te^{128}	127·936	Tl^{203}	203·036
N^{15}	15·007	Zn^{64}	63·937	Cs^{133}	132·933	Tl^{205}	205·037

H^2, now called D, was determined originally by K. T. Bainbridge [20] as 2·01351 and by J. D. Hardy, E. F. Barker, and D. M. Dennison [20] as 2·01367; more recently [21] the first has redetermined it as 2·01363 ± 0·00004 with reference to He^4 = 4·00216 and 2·01363 ± 0·00008 with reference to O^{16} = 16·0000. The determinations of

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[16] *Ann. Reports*, 1928, **25**, 314.

[17] *Ibid.*, 1930, **27**, 316.

[18] H. Kallman and W. Lasarev, *Z. Physik*, 1933, **80**, 237; *A.*, 333; F. W. Aston, "Mass Spectra and Isotopes," London, 1933; M. Ashley and F. A. Jenkins, *Physical Rev.*, 1931, [ii], **37**, 712; 1932, **42**, 438; *A.*, 204, 1223; *Ann. Reports*, 1932, **29**, 303.

[19] *Ibid.*, 1928, **25**, 304.

[20] *Ibid.*, 1932, **29**, 302.

[21] *Physical Rev.*, 1933, [ii], **43**, 103; **44**, 57; *A.*, 203.

H^1 as 1·007775 and of Li^6, Li^7, Be^9, B^{11}, Ne^{20}, and Ne^{22} were also done by him.[22] A. McKellar [23] has done Li^6 and Li^7. A. S. King and R. T. Birge [24] did C^{13}, R. T. Birge [25] N^{15} and O^{17}, and H. D. Babcock and R. T. Birge [26] O^{18}. The remainder have been done by F. W. Aston.[27]

The abundances of the rarer isotopes of the light elements have generally been under-estimated in preliminary work; most of the redeterminations of the abundance ratios of common to rarer isotope have given smaller values. The change in the ratio H : D from 35,000 to 5,000 has already been discussed.[28] K. T. Bainbridge [29] concluded that 11·3 is the most probable value for $Li^7 : Li^6$. L. S. Ornstein and J. A. Vreeswijk, jun.,[30] found 4·43 from band spectrum work for $B^{11} : B^{10}$; earlier values ranged from 3·63 to 4·86. The ratio $C^{12} : C^{13}$ formerly given [31] as 650 and 400 is now found to be as small as 106 by F. A. Jenkins and L. S. Ornstein [32] from band spectrum work on $C^{12}C^{13}$ and $C^{12}C^{12}$. (The calculated atomic weight of carbon on this ratio is 12·01, a value greater than the International value but the same as the latest determination, 12·011, of M. Woodhead and R. Whytlaw-Gray.[33]) For $N^{14} : N^{15}$, R. T. Birge and D. H. Menzel [34] found 320, H. M. Urey and G. M. Murphy [35] 347; these are about half the original estimates. There has been no change [18, 34] in the most important of these ratios, that of $O^{16} : O^{18}$. For gallium the ratio $Ga^{69} : Ga^{71}$ calculated from optical evidence [36] is 1·5, a result which leads to an atomic weight in excellent accord with the experimental value.

In the main, atomic weights [37] calculated from mass-spectrographic data are now in good accord with those determined directly. Where there have been differences the values got by the former method have generally prevailed, and that despite the three-fold disadvantage that its accuracy is not greater than 1 in 10^5, that the conversion factor from the scale $O^{16} = 16{\cdot}0000$ to the scale $O = 16{\cdot}0000$ introduces an error as large, and that there are inherent uncertainties in the degree of precision in the measurement of abundance ratios. The principal battleground between physical and chemical methods of determining atomic weights during the period has been the Katanga deposits of pitchblende, the work on which is discussed in the section on Atomic Weights.[38] The discrepancies found by such careful and experienced workers show clearly how unwise it is to deduce the abundances of different lead isotopes from chemical determinations of atomic weights, and this probably applies generally. Recent work on the atomic weight of potassium [39] supports this point.

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[22] *Physical Rev.*, 1933, [ii], **43**, 424; **44**, 56; *A.*, 442.

[23] *Ibid.*, **44**, 155; *A.*, 994.

[24] *Astrophys. J.*, 1930, **72**, 19; *A.*, 1931, 15.

[25] *Physical Rev.*, 1931, [ii], **37**, 841; *A.*, 204.

[26] *Ibid.*, 233; *A.*, 203.

[27] *Ann. Reports*, 1930, **27**, 305; 1932, **29**, 301. "Mass Spectra and Isotopes," London, 1933.

[28] This vol., p. 30.

[29] *J. Franklin Inst.*, 1931, **212**, 317; *A.*, 1931, 1201.

[30] *Z. Physik*, 1933, **80**, 57; *A.*, 204.

[31] *Ann. Reports*, 1930, **27**, 306.

[32] *Proc. K. Akad. Wetensch. Amsterdam*, 1932, **35**, 1212; *A.*, 333.

[33] *J.*, 1933, 846; *A.*, 894.

[34] *Physical Rev.*, 1931, [ii], **37**, 1669; *A.*, 204.

[35] *Ibid.*, **38**, 575.

[36] J. S. Campbell, *Nature*, 1933, **131**, 204; *A.*, 334.

[37] *Ber.*, 1933, **66**, [*A*], 21; *A.*, 203.

Many results have been obtained by F. Allison and the Alabama school of workers [40] with their magneto-optic method of determining isotopes, but it is not yet time to discuss them fully here. The method itself consists in observing the Faraday magneto-optical rotation produced by solutions of metallic salts, and measuring the lag between the application of the field and the appearance of the optical effect. Even with very dilute solutions it is claimed that the presence of a particular isotope makes itself evident by the occurrence of a particular lag. The existence of these lags has been confirmed by W. M. Latimer and H. A. Young,[41] who had no difficulty in finding a new isotope H^3 along with D and H. Others, however, have thrown doubt even on the very existence of the time-lags; and there is no doubt of the wrongness of their interpretation. In the same laboratory G. N. Lewis and F. H. Spedding [41] had found no optical evidence of H^3 in a hydrogen–diplogen mixture; if it exists at all, it is present at a concentration below 1 in 6×10^6. Bismuth, whose single isotope, Bi^{209}, is in accord with work on radioactivity, on chemical atomic weights, and on mass-spectrography, is reported [40] as having, in decreasing order of abundances, the isotopes 211, 210, 209, 212, 215, 214, 213, 216, 207, 205, 206, 208, 219 and 217, and thallium (atomic weight 204·4; Tl^{205} and Tl^{203} in the ratio of 12 : 5) the masses 207, 205, 211, 203, 201, 209, 215, 213. As a matter of arithmetic these results lead to absurd values of atomic weights. Less pretentious but hardly more plausible lists have been given for cobalt, lead, elements 85 and 87, thorium, uranium, and other metals. Their existence is the best evidence of the untrustworthiness of this interpretation of the time-lags.

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[38] See this vol., p. 84.

[39] See this vol., p. 85.

[40] *Physical Rev.*, 1931, [ii], **37**, 1178; 1932, **40**, 1015; 1933, **43**, 38, 43, 47, 48, 49; *A.*, 204, 241, 1223; *J. Amer. Chem. Soc.*, 1933, **55**, 3207, 4370; *A.*, 994; **1934, 5.**

[41] *Physical Rev.*, 1933, [ii], **44**, 690; **43**, 964; *A.*, 759.

Artificial Disintegration by Swift Protons, Diplons, Neutrons, and α-Particles.

Four projectiles essentially different are now available for revealing the structure of the nuclei of the lighter elements by the effects they produce on bombardment. J. D. Cockcroft and E. T. S. Walton[42] have continued their work[43] on the bombardment of lithium, boron, and other nuclei with protons accelerated at high voltages. Lithium on disintegration yields a group of particles of range less than 2 cm. and a homogeneous group of range 8·4 cm. The process corresponding with the latter is believed to be $H + Li^7 \longrightarrow 2He^4$. From boron one α-particle per 2×10^6 incident protons at 500,000 volts was obtained. The energies found support the view that a proton is captured by the B^{11} nucleus, which then splits into three α-particles: $H + B^{11} \longrightarrow 3He^4$. E. O. Lawrence, M. S. Livingston, M. C. Henderson, and M. G. White[44] confirmed both the lithium and the boron results and found some evidence in addition of the disintegration of aluminium by swift protons. M. L. E. Oliphant and (Lord) Rutherford[45] have extended this work. Lithium and boron in very thin films were bombarded by protons accelerated at quite low voltages (20,000—200,000 volts). The former gave off α-particles when struck by 30,000-volt protons; the latter did not do so until the protons were at 60,000 volts. Beryllium and fluorine were similarly disintegrated but to a markedly smaller extent. No disintegration was observed with targets of nitrogen, oxygen, sodium, aluminium, iron, gold, thallium, lead, bismuth, thorium, or uranium with protons accelerated up to 200,000 volts; earlier observations[43] on aluminium, uranium, and other elements are ascribed to contamination by boron from the glass of the apparatus. The disintegration of B^{11} is confirmed as consisting in the absorption of the proton, followed by a split into three α-particles. The most probable mode of disintegration is a symmetrical escape of the particles with equal velocities. The energy which becomes available in this change (9×10^6 volts) is similar to that calculated from the masses of the particles.

The diplon has now become an important projectile. E. O. Lawrence, D. H. Sloan, and M. S. Livingston[46] had developed an apparatus for obtaining high-speed ions corresponding with more than a million volts in energy. With G. N. Lewis and M. C. Henderson [47] they found that diplons were much more effective than protons of equal energy in causing transformations in a number of elements. From lithium bombarded by diplons, α-particles were ejected with a greater velocity than any yet observed from radioactive elements. The diplon is captured by the Li^6 nucleus and the resultant breaks into two α-particles, which escape in nearly opposite directions: $D + Li^6 \longrightarrow 2He^4$. They bombarded beryllium and nitrogen (in ammonium nitrate) and obtained α-particles, but the processes thought to have occurred have not yet been formulated. There were similar rare disintegrations with magnesium and aluminium. They noticed that protons of 18-cm. range were produced when the molecular diplon ions struck any target whatever; they suggest that the diplon may break up into a proton and a neutron: $D \longrightarrow H + n$, either in the bombarded nucleus or in the strong field in its neighbourhood. If this occurs, however, and the conservation of energy holds, the mass of the neutron should be less than J. Chadwick's estimate [48]: 1·0006 instead of 1·0067. Expressed in another way, the difference between the masses of D, 2·0136, and of n + H, 2·0145, corresponds with a binding energy less than 10^6 volts. If this were all, the diplon would very probably be broken by collision with swift α-particles; preliminary experiments on this effect, however, do not support this suggestion.[49] They also found that neutrons were produced by the disintegration of Be^9 either by capturing a diplon, $D + Be^9 \longrightarrow n + B^{10}$, or by merely disintegrating the beryllium nucleus. The latter was the more likely, as the probability of the disintegration of Be^9 was found to be independent of the energy of the diplon. This process furnishes an excellent supply of neutrons for purposes of investigation. M. L. E. Oliphant, B. B. Kinsey, and (Lord) Rutherford [50] with their technique [45] have confirmed and extended some of these results. The α-particles ejected from lithium by diplons fall into two groups: one of 13·0 cm. range and 11·5 × 10^6 volts energy and another which contains particles of energies from 1·7 to 8·3 × 10^6 volts. The former probably arises from the transformation $D + Li^6 \longrightarrow 2He^4$, the latter from $D + Li^7 \longrightarrow 2He^4 + n$. The maximum energy of the neutron may be as high as 15 × 10^6 volts. They examined also the short-range particles emitted when protons strike lithium; [42] these may include two groups of ranges 6·5 mm. and 11·5 mm.

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[42] *Nature*, 1933, **131**, 23; *A.*, 111.
[43] *Ann. Reports*, 1932, **29**, 307.
[44] *Physical Rev.*, 1932, [ii], **42**, 150; 1933, **43**, 98, 304, 369; *A.*, 1932, 554; 1933, 204, 1225.
[45] *Proc. Roy. Soc.*, 1933, [*A*], **141**, 259; *A.*, 883.
[46] *Physical Rev.*, 1931, [ii], **38**, 2021; 1932, **40**, 19; *A.*, 1932, 106, 554.

[47] *Physical Rev.*, 1933, [ii], **44**, 55, 56, 781, 782. [48] *Ann. Reports*, 1932, **29**, 306.
[49] (Lord) Rutherford, *Nature*, 1933, **132**, 955.
[50] *Proc. Roy. Soc.*, 1933, [*A*], **141**, 722; *A.*, 1100.

P. I. Dee and E. T. S. Walton,[51] using camera and expansion chamber, have confirmed the processes, $H + Li^7 \longrightarrow 2He^4$ and $D + Li^6 \longrightarrow 2He^4$, with a different technique and with much higher potentials (up to 400,000 volts), and discussed the processes. The proton emission from lithium on bombardment with diplons has been extended to carbon and iron by J. D. Cockcroft and E. T. S. Walton;[42, 49] their diplons were accelerated to about 500,000 volts; they did not observe proton emission from copper or gold. The neutron emission from lithium bombarded by diplons has been confirmed by H. R. Crane, C. C. Lauritsen, and A. Soltan.[52] They found also that beryllium gave neutrons readily when the diplons were accelerated up to 900,000 volts; the process is formulated as $D + Be^9 \longrightarrow n + B^{10}$. The kinetic energy of the issuing neutrons was about 9×10^6 volts; the yield was several hundreds of times greater than that obtained by the method with which they were discovered.[53]

Relative to the diplon the neutron has been neglected as a projectile. W. D. Harkins, D. M. Gans, and H. W. Newson [54] found evidence in Wilson photographs of the disintegration of nitrogen by neutrons from beryllium struck by rays from a mesothorium preparation. The neutron was captured; the resulting nucleus then split according to $n + N^{14} \longrightarrow N^{15} \longrightarrow He^4 + B^{11}$. Fluorine and neon were also disintegrated; the former process is possibly $n + F^{19} \longrightarrow He^4 + N^{16}$, the latter $n + Ne^{20} \longrightarrow He^4 + O^{17}$. These results confirm and extend those of N. Feather [48] with a similar technique. He [55] has examined the tracks of neutrons in oxygen, and in oxygen–hydrogen and acetylene–helium mixtures. Most of the neutrons (from a polonium beryllium source) have an upper energy limit of about $4{\cdot}5 \times 10^6$ volts. Disintegrations were observed in oxygen, confirming the original work: $n + O^{16} \longrightarrow He^4 + C^{13}$; the energy relations required in addition the production of a γ-ray of high energy. The disintegration of carbon by neutrons is very rare, if existent.

The conditions of emission of neutrons by the bombardment of light atoms with α-particles from polonium have been determined by (Mme.) I. Curie and F. Joliot.[56] Beryllium and boron yield neutrons most readily (confirming the original work of J. Chadwick),[48] lithium comes next, then fluorine, sodium, and aluminium. With beryllium and boron a minimum energy of the α-particle was required to excite the target; as the energy increased, the excitation first rose to a maximum and then dropped to a minimum. The energies at maximum excitation were 26×10^6 volts for beryllium and $2{\cdot}2 \times 10^6$ volts for boron. With lithium γ-rays were emitted when the α-particle was at 3×10^6 volts, and neutrons when it was at 5×10^6 volts. It appears [57] that α-particles of comparatively low velocities penetrate the nucleus by a resonance process and that swift α-particles enter over the top of its potential barrier. No penetrating radiation was found [56] when hydrogen, carbon, nitrogen, oxygen, phosphorus, and calcium were bombarded with α-particles. G. Kirsch,[58] who had earlier [59] found proton emission from α-particle bombardment, where others had failed to observe it, found small neutron emission in the bombardment by α-particles from polonium of carbon, nitrogen, magnesium, aluminium, sulphur, iron, nickel, copper, zinc, molybdenum, palladium, arsenic, tin, tungsten, platinum, gold, and lead; lithium, beryllium, and boron were found to give strong emission. He thus confirms the work of (Mme.) I. Curie and F. Joliot on aluminium (but apparently not on fluorine and sodium) and differs from them on nitrogen and oxygen. P. Auger and G. M. Herzen,[60] using the Wilson method, have also confirmed the emission of neutrons from aluminium; this is very small compared with that from beryllium under similar conditions. If nitrogen and oxygen be confirmed as emitting neutrons, this property must be assigned to N^{15} and O^{17} and O^{18}, not to the common atoms, for in all known nuclei the atomic mass is never less than twice the atomic number, and this condition would be violated by the nuclei formed from N^{14}, O^{16} (and He^4) if these atoms emitted a neutron under α-particle bombardment. For some elements γ-rays accompany neutron emission; with others protons accompany neutrons. The disintegration of beryllium, for example, may lead to a swift neutron or to a slower neutron accompanied by a γ-ray of high energy. From fluorine or aluminium both protons and neutrons may be emitted; as these elements are isotopically simple, the emission processes are alternative.

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[51] *Proc. Roy. Soc.*, 1933, [*A*], **141**, 733; *A.*, 1100; *Nature*, 1933, **132**, 818; *A.*, 1934, 5.

[52] *Physical Rev.*, 1933, [ii], **44**, 692, 783; *Compt. rend.*, 1933, **197**, 639, 913; *A.*, 1225; 1934, 6.

[53] *Ann. Reports*, 1932, **29**, 305.

[54] *Physical Rev.*, 1933, [ii], **43**, 203, 236; **44**, 529, 945; *A.*, 1225.

[55] *Proc. Roy. Soc.*, 1933, [*A*], **142**, 689; *A.*, 1934, 6.

[56] *Compt. rend.*, 1933, **196**, 397; *A.*, 335; *J. Phys. Radium*, 1933, [vii], **4**, 21, 278; *A.*, 335, 883.

(Frl.) L. Meitner and K. Philipp [61] have studied the connexion between neutrons and the accompanying γ-rays by the Wilson method. They think it probable that neutrons and γ-rays are emitted simultaneously. They have emphasised the fact that some nuclear processes can be carried out in both directions; *e.g.*, $He^4 + B^{11} \rightleftharpoons n + N^{14}$.

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[57] J. Chadwick, *Proc. Roy. Soc.*, 1933, [*A*], **142**, 1; *A.*, 1224.
[58] *Naturwiss.*, 1933, **21**, 332; *A.*, 659.
[59] *Ann. Reports*, 1926, **23**, 285.
[60] *Compt. rend.*, 1933, **196**, 543; *A.*, 335.
[61] *Naturwiss.*, 1932, **20**, 929; *A.*, 110.

When the neutron was discovered it was not regarded as a fundamental particle because it could be represented as $n = H + e$. The existence of the positive electron, however, suggests that n or H is fundamental since now H itself can be represented as $n + e^+$. (Mme.) I. Curie and F. Joliot [62] have found that positive electrons may result from the bombardment of aluminium and boron (though not of lithium, carbon, or silver) by α-particles, as well as protons and neutrons. If these emissions are simultaneous, there is a possibility that a proton has broken up into a neutron and a positive electron, *i.e.*, $H = n + e^+$. On this view the transformation of B^{10} would be $He^4 + B^{10} = C^{13} + n^1 + e^+$ or $= C^{13} + H$ simultaneously. Taking account of the energies involved, this leads to a mass of the neutron 1·011, which is greater than J. Chadwick's estimate; there are other difficulties also in getting masses and energies to balance. This question, which is part of the complex question of the structure of light nuclei, has been discussed by J. Chadwick,[57] W. Heisenberg,[63] and many others, and has been extended to the diplon, which may be a union of proton and neutron as suggested by the above experiments describing its break up.[47] This possibility has been strengthened by different evidence. D. E. Lea [64] studied the scattering of neutrons by hydrogen and other gases and found a γ-ray effect in hydrogen only which might be interpreted as resulting from the combination of neutron and proton to form diplon in some of the collisions. The different schemes suggested [65] may be represented as $H = n + e^+$, $n = H + e$, $n = H + d$; $D = 2H + e$, $D = 2n + e^+$, $D = H + n$ (H = proton, D = diplon, e = electron, e^+ = positive electron, n = neutron, d = Dirac's electron of negative energy). It is obvious that no decision on these points can be formed in the present tentative position both of experimental work and of theory. New particles may still be discovered (*e.g.*, a neutron [66] of mass 2) whose existence may profoundly modify present speculative theory; the fact that difficulties await solution is a powerful incentive to obtain great accuracy in the determination of the masses and energies involved in the transformation of light atoms by bombardment with the various projectiles.

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[62] *Compt. rend.*, 1933, **196**, 1885; **197**, 237; *A.*, 762, 883.

[63] *Z. Physik*, 1932, **77**, 1; **78**, 156; *A.*, 1932, 894, 1074.

[64] *Nature*, 1934, **133**, 24.

[65] W. D. Harkins, *J. Amer. Chem. Soc.*, 1933, **55**, 855; *A.*, 334; D. Meksyn, *Nature*, 1933, **131**, 366; W. Elsasser, *ibid.*, p. 764; *A.*, 658; N. Thon, *ibid.*, p. 878; *A.*, 762; G. W. Todd, *ibid.*, **132**, 65; *A.*, 883; T. Sexl, *ibid.*, p. 174; *A.*, 995; R. M. Langer, *Science*, 1932, **76**, 294; *A.*, 1932, 1187; E. N. Gapon, *Z. Physik*, 1933, **84**, 509, 520; *A.*, 995; R. Fürth, *ibid.*, **85**, 294; *A.*, 1100; J. J. Placinteanu, *ibid.*, **84**, 370; *A.*, 995; *Compt. rend.*, 1933, **196**, 1474; **197**, 549; *A.*, 660, 995; H. R. von Traubenberg, *Naturwiss.*, 1932, **20**, 934; *A.*, 111; J. Perrin, *Compt. rend.*, 1933, **197**, 628; *A.*, 1224.

In Table III are summarised the principal disintegration processes which occur with light elements. These include (for the sake of comparison and completeness) old results [67] for proton emission from light elements bombarded by α-particles. Where masses are unknown or obvious they are omitted. In each scheme the symbol for the projectile precedes that of the target; the symbol of the more certainly recognised disintegration product follows the arrow.

TABLE III.

Process.	Reference.	Process.	Reference.
$H+Li^7 \longrightarrow 2He^4$	42, 43, 44, 45, 50, 51	$He^4+B^{11} \longrightarrow n+N^{14}$	48, 56, 58
		$He^4+N^{14} \longrightarrow H+O^{17}$	67
$H+Be^9 \longrightarrow He^4+\ ?$	45	$He^4+F^{19} \longrightarrow H+Ne^{22}$	67
$H+B^{11} \longrightarrow 3He^4$	42, 44, 45	$He^4+F^{19} \longrightarrow n+\ ?$	56, 57
$H+F^{19} \longrightarrow He^4+\ ?$	45	$He^4+Ne \longrightarrow H+Na$	67
$D+Li^6 \longrightarrow 2He^4$	47, 50, 51	$He^4+Na^{23} \longrightarrow H+Mg^{26}$	67
$D+Li^7 \longrightarrow n+2He^4$	50, 52	$He^4+Na^{23} \longrightarrow n+\ ?$	56, 57
$D+Be^9 \longrightarrow n+B^{10}$	47, 52	$He^4+Mg \longrightarrow H+Al$	67
$D+Be^9 \longrightarrow He^4+\ ?$	47	$He^4+Al^{27} \longrightarrow H+Si^{30}$	67
$D+N^{14} \longrightarrow He^4+\ ?$	47	$He^4+Al^{27} \longrightarrow n+\ ?$	56, 58, 60
$n+N^{14} \longrightarrow He^4+B^{11}$	52, 59, 65	$He^4+Al^{27} \longrightarrow e^{+}+\ ?$	62
$n+O^{16} \longrightarrow He^4+C^{13}$	52	$He^4+Si \longrightarrow H+P$	67
$n+F^{19} \longrightarrow He^4+\ ?$	54	$He^4+P^{31} \longrightarrow H+S^{34}$	67
$n+Ne^{20} \longrightarrow He^4+O^{17}$	54	$He^4+S \longrightarrow H+Cl$	67
$He^4+Li^7 \longrightarrow n+B^{10}$	56, 58	$He^4+Cl \longrightarrow H+A$	67
$He^4+Be^9 \longrightarrow n+C^{12}$	48, 56, 58	$He^4+A \longrightarrow H+K$	67
$He^4+B^{10} \longrightarrow H+C^{13}$	67	$He^4+K \longrightarrow H+Ca$	67
$He^4+B^{10} \longrightarrow n+e^{+}+C^{13}$	62		

The Positive Electron.

The positive electron was discovered independently by C. D. Anderson [68] and by P. M. S. Blackett and G. P. S. Occhialini [69] in an investigation of the penetrating or cosmic radiation by the cloud method.[70] Amongst the tracks of the particles of very great energy included in or produced by this radiation were found some which differed mainly from the tracks of electrons in being curved by a magnetic field in the opposite direction. Anderson[71] found 15 out of 1300 cosmic-ray tracks whose curvature and ionisation suggested a positive particle much smaller than a proton, in fact, of mass not more than twenty times that of an electron. Later he concluded that positive and negative electrons were within 10% of each other in charge and 20% in mass. Blackett and Occhialini found substantially the same. An interesting feature of the numerous photographs taken was the existence of "showers" or multiple pairs of particles of opposite sign due apparently to some nuclear disintegration process stimulated by particles of high energy in the cosmic radiation. The discovery of terrestrial sources of positive electrons which followed quickly on the other has led to their investigation under more controlled experimental conditions. Positive electrons are produced by the absorption by matter (*e.g.*, lead) of the penetrating γ-radiation[72] from radio-elements (*e.g.*, from thorium-C'') or of the penetrating radiation[73] (in part neutrons, in part γ-radiation) produced by the impact of α-particles on beryllium. They are also produced[62] in what may be a nuclear transformation by the impact of α-particles on aluminium and boron. When quanta produce positive electrons on their absorption in matter, preliminary work[74] shows that the number increases rapidly with the energy of the quanta and with the atomic number of the absorber. From this it has been deduced that the effective area for the production of a positive electron is a little larger than the area of cross-section of the nucleus. The maximum energy of the positive electron produced by a given radiation seems to be the same for all absorbers, and this, also, makes it unlikely that the production of positive electrons is a nuclear process.

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[66] H. Walke, *Nature*, 1933, **132**, 242; *A.*, 995.

[67] (Lord) Rutherford, J. Chadwick, and C. D. Ellis, "Radiations from Radioactive Substances," Cambridge, 1930.

[68] *Science*, 1932, **76**, 238.

[69] *Proc. Roy. Soc.*, 1933, [*A*], **139**, 699; *A.*, 441.

[70] *Ann. Reports*, 1932, **29**, 314.

It is obvious that if quanta alone produce positive electrons, and do so outside the nucleus, the discussion is simplified. (Mme.) I. Curie and F. Joliot[73] have shown that it is the γ-radiation in the mixed radiation produced by α-particles on beryllium which produces the positive electrons; on the other hand, in their nuclear-transformation experiments[62] they suggest that positive electrons originate in the nucleus. P. M. S. Blackett,[74] however, has interpreted them otherwise; the positive electron may be produced outside the nucleus by the internal conversion of a γ-ray emitted by it. If the positive electron is produced outside the nucleus, it follows that, as there is no place in atomic theory for its permanent existence, a positive electron cannot arise without the simultaneous production of a (negative) electron. This conclusion is in accord both with experimental observation of the pairs of tracks and with determinations of the maximum energies of the positive and negative electrons in their tracks. The occurrence of the reverse process, namely, the production of a single quantity of radiation by a positive and a negative electron, is a necessary consequence of the process just stated. The theory in this tentative form is akin in one way to the " neutral pair " theory of the γ-ray of (Sir) W. H. Bragg,[75] which was abandoned later for the wave-theory. He imagined an electron as capable of attracting to itself sufficient positive electricity to neutralise its own charge and of doing this without appreciable addition of mass. (This is the transformation β-particle $\longrightarrow \gamma$-ray.) The reverse process was believed to occur when the electron put down its positive charge again. Neither change was thought to take place except when an entity traversed an atom. Blackett and Occhialini interpret their work on P. A. M. Dirac's theory[76] of " holes." Dirac deduced from the wave-equation obtained from the relativity quantum theory of an electron that states are possible in which electrons should possess negative kinetic energies. He dealt satisfactorily with the paradoxes which this view entails. He assumed that there are so many electrons in the world that all the states of negative energy except perhaps a few are occupied, and supposed that the infinite number of electrons present in any volume will remain undetectable if they are uniformly distributed; only an unoccupied state or " hole " would correspond with an observed particle. These should behave in an external field like particles with the same mass and spin as an electron but with a positive charge. (These were at the time identified with protons, but the difficulty of explaining why protons differed so widely in mass from electrons was recognised.) The experimental discovery of the positive electron has thus greatly strengthened Dirac's theory and extended the field of phenomena over which it may be applied. J. R. Oppenheimer and M. S. Plesset[77] have calculated from it the probability of production of pairs of electrons of opposite charge when penetrating γ-rays are absorbed by matter.

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[71] *Physical Rev.*, 1933, [ii], **43**, 491; **44**, 406; *A.*, 441, 1100.

[72] C. D. Anderson, *Science*, 1933, **77**, 432; C. D. Anderson and S. H. Neddermeyer, *Physical Rev.*, 1933, [ii], **43**, 1034; (Mme.) I. Curie and F. Joliot, *Compt. rend.*, 1933, **196**, 1581; *A.*, 658; (Frl.) L. Meitner and K. Philipp, *Naturwiss.*, 1933, **21**, 468; *A.*, 762; C. Y. Chao and T. T. Kung, *Nature*, 1933, **132**, 709; (Lord) Rutherford, *ibid.*, p. 709; *A.*, 1934, 5.

[73] *Compt. rend.*, 1933, **196**, 1105; *A.*, 549; see also J. Chadwick, P. M. S. Blackett, and G. P. S. Occhialini, *Nature*, 1933, **131**, 473; *A.*, 441; (Frl.) L. Meitner and K. Philipp, *Naturwiss.*, 1933, **21**, 286; *A.*, 550.

[74] *Nature*, 1933, **132**, 917; M. Grinberg, *Compt. rend.*, 1933, **197**, 318; *A.*, 883.

[75] *Ann. Reports*, 1909, **6**, 242.

[76] *Ibid.*, 1930, **27**, 325.

[77] *Physical Rev.*, 1933, [ii], **44**, 53, 948.

The calculated are in good agreement with the experimental results. They regard the absorption of γ-rays by atoms resulting in the production of pairs of oppositely charged electrons as a photoelectric absorption by electrons with negative kinetic energy—" virtual " electrons—near the nucleus. G. Beck [78] has calculated the number of these which are effective for absorption; it is proportional to the square of the atomic number and is small; lead has about one. He has indicated also that the place of production is outside the nucleus but within the K-ring. Many experiments have been done on this subject and it has been widely discussed.[79] Dirac's theory has not yet explained the production of the multiple pairs which form the showers.

The relation of positive electrons to the cosmic radiation is still imperfectly known. Certain facts, however, have been established by Anderson,[80] Blackett and Occhialini,[69] P. Kunze,[81] and T. H. Johnson : [82] half the fast particles which produce cosmic ray ionisation at sea-level are positive electrons, half are electrons; the same ratio occurs in the " showers "; the majority of the particles incident on the earth's atmosphere are positively charged, probably positive electrons, not protons.

The Penetrating Radiation.

Investigations of widely-different character—cloud-chamber experiments,[74] absorption of the penetrating rays with the Bothe–Kolhörster double counter, measurements of the relative intensity of the radiation at different parts of the earth,[83] and determination of its intensity at different heights in the atmosphere and depths in water [84]—all now support the view that the penetrating radiation at high altitudes consists of electrified particles produced in the atmosphere or entering it from remote space. (At lower altitudes a mixture of particles and photons is likely to be present in the radiation, the latter being produced by the former by processes similar to the production of X-rays by an electron.) The supposed invariance[85] of the distribution of the radiation with latitude, implying that the earth's magnetic field does not affect the radiation, was the one strong piece of evidence against the particle theory. Actually, however, there is variation.[83] At temperate and polar latitudes (from 50° N. and S. to the poles) the radiation is nearly constant and more intense than in tropical latitudes; the differences are about 14, 22, and 33% at sea-level, 2000, and 4000 metres respectively. The extensive experiments which have been carried out at high altitudes by sounding and passenger balloons, and on high mountains, support the particle theory also. The data show a rapid increase in intensity of the radiation with altitude; it continues nearly exponentially to a height of 15 km. and above that approaches a limiting value; there is apparently no detectable decrease in ionisation as the top of the atmosphere is approached. Quite different results are to be expected if the radiation consist appreciably of photons. The ionisation is constant in time to within 2% at any one place. As has been said, the majority of the particles high in the earth's atmosphere are positively charged and are probably positive electrons. Their energy is of the order of 10^{10} volts. At sea-level half the particles are electrons, half positive electrons; their energies vary from a few million to nearly 10^{10} volts. They are accompanied by photons which are probably the precursors of the single pair and multiple pairs of oppositely charged electrons observed in the cloud-chamber apparatus.

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[78] *Z. Physik*, 1933, **83**, 498; *A.*, 884.

[79] W. H. Furry and J. F. Carlson, *Physical Rev.*, 1933, **44**, 237; (Mme.) I. Curie and F. Joliot, *J. Phys. Radium*, 1933, [vii], **4**, 494; *A.*, 1224; D. Skobeltzyn, *Nature*, 1934, **133**, 23.

[80] *Physical Rev.*, 1932, [ii], **41**, 405.

[81] *Z. Physik*, 1933, **80**, 559; **83**, 1; *A.*, 763.

[82] *Physical Rev.*, 1933, [ii], **43**, 1059.

[83] J. Clay, *Proc. K. Akad. Wetensch. Amsterdam*, 1932, **35**, 1282; *A.*, 335; A. H. Compton, *Physical Rev.*, 1933, [ii], **43**, 28; *Nature*, 1933, **131**, 713; *Science*, 1933, **77**, 480; *A.*, 660.

[84] E. Regener, *ibid.*, 1932, **130**, 364; 1933, **132**, 696; *Physikal. Z.*, 1933, **34**, 306; *A.*, 552.

The origin of the radiation remains quite obscure. If it comes from outside and is mainly positive electrons, it can be calculated[86] that the total mass of the radiation in the universe is staggeringly enormous—about 0·1% of the mass of all the stars and nebulæ. On the other hand, the only terrestrial source that has been suggested[87] is thunderstorms, and there the main difficulties have been the constancy of the intensity with time and its very high energy. The last is evidence that it does not arise from a nuclear process. The constancy with time rules out the sun, and presumably therefore the stars, as a source. There is, further, nothing in the cold of empty space likely to produce a radiation which has failed to appear in the greater cold of the laboratory. At the present time the evidence for the radiation points to an unknown terrestrial source.

A. S. RUSSELL.

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[85] *Ann. Reports*, 1932, **29**, 315.

[86] G. Lemaître, *Nature*, 1931, **128**, 704.

[87] C. T. R. Wilson, *Proc. Camb. Phil. Soc.*, 1925, **22**, 534.

CRYSTALLOGRAPHY.

CRYSTALLOGRAPHIC research in the last two years has no longer been primarily concerned with structure determination. The main types of structure have already been determined, and the more complicated structures are found in general to be variations on simpler types or combinations between them. The prevailing interest has shifted to the relations between crystal structure and physical properties, and to relations and transformations between crystal types. Crystal physics more firmly grounded on quantum mechanics is widening its scope and becoming increasingly quantitative and precise, whilst crystal chemistry is appearing more and more as the basis on which the chemistry of the future will be written. The rational chemistry of metals and ores is a creation of structural crystallographic methods; the chemistry of cellulose and other complex polymerides such as the proteins has through them made a critical advance.

The appearance of the first volume of " The Crystalline State," a general survey by W. L. Bragg, has at last provided an authoritative, attractive, and simple presentation of the contribution of structure analysis to the problems of physics, chemistry, biology, and technics. This volume is not intended for specialists in the field, but should be in the hands of every chemist who wishes to do original work on modern lines.

Ewald's new edition of " Die Erforschung des Aufbaues der Materie mit Röntgenstrahlen " furnishes a more theoretical approach to the problem of crystal analysis: it is particularly valuable for its account of X-ray optics.

The Properties of Cuprous Oxide.—The commercial use of rectifiers and photocells based on the remarkable properties of semi-conducting crystalline films of cuprous oxide (cuprite) has drawn much attention to the electrical and optical behaviour of this substance. An excellent review of this field until the end of 1932, with copious references, is given by L. O. Grondahl,[1] which leads us to conclude that the theoretical side of the subject is not as far advanced as the practical.

Cuprous oxide, as a large single crystal, has a slight electrical conductivity which appears to depend on the concentration of free oxygen which it contains.[2] When the crystal is illuminated, a photoconductivity appears (inner photoelectric effect),[3] photoelectrons are ejected from the surface (outer photoelectric effect) and a potential difference may be set up between different parts of the crystal, as if electrons had been carried in the direction of the light rays[4] (Dember effect). Photoconductivity is, of course, a usual phenomenon with non-conducting crystals (for a general review of the subject see F. C. Nix[5]); the outer photoelectric effect is well known in metals, but little work seems to have been done on it for less good conductors.[6] The measurement of the photoconductivity is not easy with cuprite, since the normal conductivity may mask the effect; recourse has been made to the use of periodic illumination, allowing the periodic current to be separately amplified;[7] and to measurements at low temperatures,[8] at which the normal conductivity is small. The technique of R. Schultze[9] with very thin films would also seem to be applicable.

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[1] *Rev. Mod. Physics*, 1933, **5**, 141.

The theoretical pictures of the passage of electrons through feebly-conducting substances have been developed by R. H. Fowler,[10] A. H. Wilson,[11] R. W. Gurney[12] and others on the basis of quantum statistics; and these pictures seem to be accepted as adequate[13] for the explanation of the inner photoelectric effect with insulating crystals. But Wilson's theory is dismissed by (Mme.) A. Joffé and A. F. Joffé[14] as unable to explain for cuprite either the potential distribution in the illuminated crystal or the variation of this potential with intensity of light. It has in fact been questioned whether, apart from the presence of impurities, semiconductors like cuprite have any real existence as such.

There seems to be some difference of opinion as to what spectral range is responsible for the photoconductivity of cuprite: thus E. Englehard [2] postulates the excitation of an infra-red absorption band, while D. Nasledov and L. Nemenov [15] even ascribe the increase of conductivity on illumination of ordinary cuprite to a heating effect. Schonwald,[7] on the other hand, finds definite photoelectric maxima at wave-lengths of 0·8, 0·63, and 0·2 Å. The simultaneous irradiation of a cuprite photocell with different wave-lengths gave non-additive effects,[16] while R. Deaglio [17] obtained a marked fatigue for the Dember effect after driving a current continuously through his crystal for six days. The indefiniteness of these data must surely be ascribed to the significant variation of electrical resistance, and even of optical absorption, with oxygen content, previously mentioned; it is not the pure crystal lattice which has been the subject of the majority of these experiments. A definite alteration of the properties of the crystal seems to have taken place after several experiments.[18]

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[2] H. Dünwald and C. Wagner, *Z. physikal. Chem.*, 1933, [*B*], **22**, 212; *A.*, 887; E. Engelhard, *Ann. Physik*, 1933, [v], **17**, 501; *A.*, 1000; G. Mönch, *Z. Physik*, 1932, **78**, 728; *A.*, 8; M. Leblanc, H. Sachse, and H. Schopel, *Ann. Physik*, 1933, **17**, 334; *A.*, 764.

[3] Pfund, *Physical Rev.*, 1916, **7**, 289; but cf. F. Waibel and W. Schottky, *Physikal. Z.*, 1932, **33**, 583; *A.*, 1932, 898.

[4] H. Dember, *ibid.*, 1931, **32**, 554, 856; 1932, **33**, 207; *A.*, 1931, 999; 1932, 8.

[5] *Rev. Mod. Physics*, 1932, **4**, 723.

[6] References in Schultze's paper (ref. 9) to work on phosphorus, aniline colours, sulphur, shellac, paraffin, water, silver halides.

[7] Schonwald, *Ann. Physik*, 1932, **15**, 395.

[8] I. Kikoin and M. Noskov, *Physikal. Z. Soviet Union*, 1933, **4**, 531.

[9] *Physikal. Z.*, 1933, **34**, 381.

[10] R. H. Fowler, *Proc. Roy. Soc.*, 1933, [*A*], **141**, 56; *A.*, 887.

[11] A. H. Wilson, *Nature*, 1932, **130**, 913; *A.*, 114.

[12] R. W. Gurney, *Proc. Roy. Soc.*, 1933, [*A*], **141**, 209; *A.*, 887.

[13] H. Teichmann, *ibid.*, **139**, 105; *A.*, 209.

[14] *Z. Physik*, 1933, **82**, 754; *A.*, 764.

The Rectifier.—When the cuprous oxide is in the form of a thin layer on a basis of metallic copper, additional phenomena make their appearance. The rectifier discs of commerce are formed by oxidising pure copper sheet at about 1000° until a layer of oxide some 0·1 mm. thick is produced. Different methods of cooling the discs lead eventually to different characteristics.[1, 19] The superficial high-resistance layer of cupric oxide is removed mechanically or by solution, and contact with the free surface of the cuprous oxide is made, *e.g.*, by rubbing it with carbon and pressing against it a thin lead disc. Such a rectifying unit has strongly asymmetrical properties; thus it may show an electrical resistance per sq. cm. with the copper positive, of 10,000 ohms, while with copper negative the value may be only a few ohms. Currents of the order of 0·1 amp. per sq. cm.—more under special conditions—and permissible voltages per disc of 10—30 volts allow the construction of cheap and reliable rectifiers of very wide application.

The theoretical explanation of the rectification is in a very confused state. Though, of course, contact rectification between crystals and point contacts (*e.g.*, the familiar wireless " crystal ") has long been known, such rectification has always been very local and precarious. The rectification of the copper–cuprous oxide disc is definitely located at the interface of the two substances (as we have seen, cuprous oxide by itself has no marked asymmetric properties), and it is the constancy of behaviour of this interface, formed, of course, from the mother copper, and protected from all contamination, which makes the commercial applications of the rectifier possible. Grondahl[1] has well summarised the theoretical position at the end of 1932, and since then there do not seem to have been any constructive suggestions for the clearing up of the difficulties. The following is a very compressed summary of his discussion.

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[15] D. Nasledov and L. Nemenov, *Z. Physik*, 1933, **81**, 584; *A.*, 554.

[16] C. Lapicque, *Compt. rend.*, 1933, **196**, 1301; *A.*, 554.

[17] *Ibid.*, p. 1303; *A.*, 554; *Z. Physik*, 1933, **83**, 179.

[18] W. Leo, *Ann. Physik*, 1932, **15**, 129; *A.*, 8.

[19] W. Bulian, *Physikal. Z.*, 1933, **34**, 745.

Attempts have been made to ascribe the rectification to thermoelectric effects; to a microscopic " point and plane " structure; to an electrolytic effect due to the presence of a more highly conducting substance between the crystals of cuprous oxide; in terms of work functions of the two substances; as due to the existence of a high-resistance thin film, deficient in electrons, between oxide and copper; as due to a cold electron emission into a thin space, largely separating oxide and copper; and in terms of the diffusion of electrons from copper into oxide, producing a " hump " of negative charge whose shape will vary with the direction of the applied potential between oxide and copper. Of these explanations, some seem to have no valid arguments in their favour, while none is able to explain completely the experimental facts.

The Photoelectric Cell.—Comparatively recently it was found that these rectifier discs, if illuminated, generated a potential difference between the electrodes.[20] The earlier experiments were made with arrangements where the light struck only the edge of the discs; later, more efficient cells were made in which the light reached the oxide layer through a semi-transparent coating, *e.g.*, of sputtered gold, which also served as the electrode, thus allowing use to be made of the whole sensitive surface. (Similar cells are now being made commercially in which selenium, rather than cuprous oxide, is the sensitive element.) Considerable electrical outputs are obtainable from such cells; thus E. D. Wilson[21] obtains one watt per sq. m. of active surface. The technique of the use and amplification of these photocurrents is very different from that appropriate to the usual vacuum or gas-filled photoelectric cell, owing to the much lower internal resistance of the source.

The properties of these cells have been widely investigated, though attempts to explain their action have not been completely successful —as one might expect, in view of the probably intimate relation between the rectifier and the photoelectric action. The emission of electrons is supposed to take place at the boundary between oxide and copper, where a " blocking layer " or " Sperrschicht " has been located by W. Schottky[22] and his followers. Such cells are called "back-wall" cells ("Hinterwand"). But in certain circumstances the photoeffect must be located at the "front wall" (Vorderwand) of the cell, *i.e.*, the boundary between the oxide and the upper (transparent) electrode; and in these cases the direction of flow of current through the cell is reversed. The assumption of a blocking-layer possessing unilateral transparency to electrons, and the transference of this layer from one side to the other of the oxide layer, according to the observed direction of flow of the current, certainly seems to be rather arbitrary. Dember thinks the blocking-layer (which is essentially regarded as a characteristic of the oxide–metal junction) to be an unnecessary assumption, in view of the photoelectric potential difference which he obtains in pure cuprous oxide crystals, as we have described; and the criticisms of E. Perucca and R. Deaglio[23] support this view. Bulian,[19] in a very interesting paper, comes to the same conclusion; he shows that the same photocell may exhibit a reversal of *E.M.F.* as its temperature is altered, or if the thickness, *i.e.*, the transparency, of the upper layer is changed. The significance seems to lie in the optical properties of the oxide layer; light for which the oxide is transparent (say $\lambda > 0{\cdot}6\ \mu$) exhibits the back-wall effect, while light to which it is more opaque gives the front-wall effect. The thickness of oxide, nature of the upper electrode, and colour of the light will decide for any particular cell which of these tendencies has the upper hand. Very similar are the conclusions of H. H. Poole and W. R. G. Atkins,[24] who explored the sensitive surface of a photocell with a small patch of light of wavelength about $0{\cdot}61\ \mu$; they found that the direction of current flow varied as the patch was moved from one point to another, and ascribed this effect to the varying opacity of the film.

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[20] Grondahl and Geiger, *Trans. Amer. Inst. Elect. Eng.*, 1927, **46**, 357; Lange, *Physikal. Z.*, 1930, **31**, 139, 964; *A.*, 1931, 9.

[21] *Electronics*, 1932, **5**, 312.

Thermal Expansion of Crystal Lattices.—Before the advent of *X*-rays, "coefficient of expansion" referred only to the behaviour of the massive substance. The question has been recently raised whether this coefficient, measured by macroscopic methods, ought necessarily to agree with the expansion deduced from the spacing of the lattice, measured by *X*-rays. If there is a difference, what is its significance? For a crystal to give a sharp *X*-ray reflexion, its lattice must be perfect over many thousands of elementary periods; but it is unlikely that this perfection is strictly maintained over the whole of any crystal of experimental size without occasional dislocations. Elsewhere in this Report reference is made to the mass of evidence concerning the "secondary structure" of crystals; arguing on the basis of this assumed structure, F. Zwicky[25] predicted that a difference between these two expansions should exist. A difference has, in fact, been reported by A. Goetz and R. C. Hergenrother[26] with single bismuth crystals. These workers claim to have shown that along the trigonal axis the X-ray expansion coefficient increased with temperature up to the melting point, but the coefficient measured optically (*i.e.*, by using interference fringes to measure the small displacements) remained constant till near the melting point, after which it decreased rapidly. They also found that the X-ray coefficients do obey Gruneisen's law,[27] whereas the optically determined ones did not. (Gruneisen's law requires an approximate proportionality between expansion coefficient and specific heat.) The discontinuities in the properties of bismuth which other workers have found at 75° and near the melting point were not detectable on the X-ray expansion coefficient curve. As an explanation it was suggested that an amorphous component coexists with the lattice, which increases relatively to the lattice with increasing temperature. On the other hand, A. H. Jay[28] finds no difference between the coefficients measured optically and by X-rays for silver and for quartz over a temperature range of 18° to 730°.*

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[22] F. Waibel and W. Schottky, *Naturwiss.*, 1932, **20**, 297; *A.*, 1932, 560; *Physikal. Z.*, 1932, **33**, 583; *A.*, 1932, 898; W. Schottky, *ibid.*, 1931, **32**, 833.

[23] *Z. Physik*, 1931, **72**, 102.

[24] *Nature*, 1933, **131**, 133; *A.*, 209.

The X-ray expansions of several hydroxides, those of magnesium, calcium, and aluminium, all layer structures, have been measured by (Miss) H. D. Megaw,[29] who finds a general anisotropy, the expansions perpendicular to the layer over a range 0—100° being greater than those parallel to the layer. In general, the measurement of lattice expansions in various directions should lead to results of significance. Thus J. B. Austin and R. H. H. Pearce[30] showed for crystals of sodium nitrate that the gradual transition occurring between 150° and 278° is marked along the c-axis, but not detectable along the a-axis. This transition they interpret as a separation of nitrate layers corresponding to a change of the vibrational energy of the nitrate ion to the rotational state. R. Becker and E. Orowan [31] find that the expansion of a single zinc crystal is not smooth, but exhibits several jumps, whose steepness increases rapidly with rise of temperature. A. Müller [32] investigated the expansion coefficients of a series of long-chain compounds from liquid-air to melting-point temperatures, and found marked differences between the coefficients measured along the three crystal axes.

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[25] *Proc. Nat. Acad. Sci.*, 1929, **15**, 253, 816; *Helv. Phys. Acta*, 1930, **3**, 629; *A.*, 1930, 139.

[26] *Physical Rev.*, 1932, **40**, 643; *A.*, 1932, 796.

[27] E. Gruneisen, *Ann. Physik*, 1912, **39**, 257; E. Gruneisen and E. Goens, *Physikal. Z.*, 1923, **24**, 506; *Z. Physik*, 1924, **29**, 141; G. Borelius and C. H. Johansson, *Ann. Physik*, 1924, **75**, 23; *A.*, 1925, ii, 27.

[28] *Proc. Roy. Soc.*, 1933, **142**, 237; *A.*, 1237.

[29] *Ibid.*, **142**, 198; *A.*, 1237.

[30] *J. Amer. Chem. Soc.*, 1933, **55**, 661; *A.*, 342.

* A. H. Jay (*Proc. Roy. Soc.*, 1934, **143**, 465) has repeated the measurements of Goetz and Hergenrother, but disagrees with their conclusions. He finds no difference between the two coefficients of expansion for bismuth, and ascribes the contrary result to experimental error.

Melting-point Phenomena.—The measurement of thermal expansions leads naturally to the drastic changes in the lattice which occur at the melting point. There is considerable evidence, of interest on the one hand to the study of liquid structure in general and on the other to the problems of nuclear formation and crystal growth, that immediately above the melting point a great deal of molecular orientation persists. This is shown by the experiments of A. Goetz [33] on the growth of single bismuth crystals, also by W. L. Webster,[34] who investigated the persistence of nuclei above the melting point for several metals, including bismuth. The nuclei showed time–temperature hysteresis effects and exhibited great differences in stability. It has also been found that crystals of erythritol, held for several minutes 1° or 2° above the melting point, will recrystallise into single crystals with approximately the same orientation as that of the original crystal.[35] The stability of crystalline nuclei in superheated melts has been considered from the kinetic standpoint by R. Bloch, T. Brings, and W. Kuhn,[36] and it is shown that they may be expected to melt more slowly, though thermodynamically they are at least as unstable as large crystals at the same temperature.

Recent evidence as to the precise temperature range over which melting-point or transition phenomena occur is rather scanty. W. L. Webster [37] showed that for bismuth the temperatures of emission of latent heat, of acquisition of rigidity, and of anomalous diamagnetic susceptibility all coincided within the experimental error of 0·3°. A. Müller [32] found remarkable changes in the lattices of the long-chain hydrocarbons "within a few tenths of a degree." The melting point of substances in a state of fine subdivision is known to be lower [38] (often as much as 10°) than that of the normal substance; but this effect is usually ascribed to some form of contamination.[39]

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[31] *Z. Physik*, 1932, **79**, 566.

[32] *Proc. Roy. Soc.*, 1930, [*A*], **127**, 417; 1932, [*A*], **138**, 514; *A.*, 116.

[33] *Physical Rev.*, 1930, **35**, 193.

[34] *Proc. Roy. Soc.*, 1933, [*A*], **140**, 653; *A.*, 767.

[35] B. W. Robinson (unpublished results).

[36] *Z. physikal. Chem.*, 1931, [*B*], **12**, 415; *A.*, 1931, 898.

[37] *Proc. Roy. Soc.*, 1931, **133**, 162; *A.*, 1931, 1221.

[38] Pawlow (1910).

We may mention the work of P. A. Thiessen and E. Ehrlich,[40] who observed the structure of the crystalline sodium salts of the long-chain fatty acids. The melting points of these acids are below those of their salts; and in each case as the salt was taken through the temperature at which the corresponding acid melted, it was found that the cooling curve showed a discontinuity and the expansion coefficient a sudden change.

Lattice Theory.—A very interesting paper by H. S. Taylor, H. Eyring, and A. Sherman[41] attempts to trace the growth of a crystal lattice from the vapour phase, *i.e.*, single atoms, applying the perturbation methods of quantum mechanics to the calculation of the energies of various possible configurations. The calculations are applied chiefly to sodium, and the binding energies, as a function of distance apart in various configurations, are evaluated for from two to eight sodium atoms. From the curves, the most probable process of growth of the lattice may be followed; a square having once been formed, the fifth atom will be added at another corner of the cube, the sixth will go to the body-centre position (where it has a considerable stabilising influence), and remaining atoms will complete the cube corners. Although these are the most probable configurations, definite amounts of energy are required for their consummation; the process of building up the lattice is difficult rather than easy, and we may expect finely divided particles and surfaces at which crystallisation is taking place to be abnormally active—as, of course, we know to be the case. The elementary cube which this calculation indicates has a unit edge of 3·4 Å. as against 4·3 Å. for massive sodium.

M. Born, J. E. Mayer, and L. Helmholtz[42, 43] have improved the general lattice theory by three variations of the energy content. The repulsion potential is expressed as an exponential term where before it was given as a power term. Van der Waals's cohesion force is also introduced into the calculation. This theory has been applied to the empirical data for the alkali halides. A very simple relation between lattice energies and ionic radii and valency has been discovered by A. F. Kapustinski[44] and applied by him and

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[39] N. Schoorl, *Proc. K. Akad. Wetensch. Amsterdam*, 1932, **35**, 378; *Z. physikal. Chem.*, 1932, [*A*], **160**, 158; *A.*, 1932, 799.

[40] *Ibid.*, 1932, [*B*], **19**, 299; *A.*, 116.

[41] *J. Chem. Physics*, 1933, **1**, 68; *A.*, 213.

[42] M. Born and J. E. Mayer, *Z. Physik*, 1932, **75**, 1; *A.*, 1932, 564.

[43] J. E. Mayer and L. Helmholtz, *ibid.*, p. 19; *A.*, 1932, 564.

[44] *Z. physikal. Chem.*, 1933, **22**, 257; *A.*, 1001.

B. Veselovski[45] to about 100 substances. If the lattice energy be plotted against $1/(r_K + r_A)$ where r_K, r_A are the radii of kation and anion respectively, then for these substances the points lie close to a straight line, so that the maximum divergence of the lattice energy from that corresponding to the straight line is about 10%. The validity of this formula makes approximate calculations very simple.

Compressibility of Crystals.—The most direct way of investigating the bonds between the atoms of a crystal lattice is, of course, to alter the distance between them by externally applied forces; but to make any perceptible effect, these forces must be very great. The masterly technique of P. W. Bridgman[46] has rendered possible accurate measurements at pressures as high as 12,000 kg./sq. cm.; a full description of the methods and precautions necessary for such work is given in his book.

If we attempt to form the equation for the potential energy in terms of position of an atom in a lattice—considering, *e.g.*, an ionic lattice of the alkali halide type—then the attractive term is usually ascribed to the electrostatic (Coulomb) forces of the oppositely charged ions, so that its form is known. E. Madelung[47] has calculated the potential energy due to this attractive force for various types of lattice. We are, however, in ignorance of the form of the repulsive term necessary to give stability to the lattice; all that we can say is that it vanishes at great distances and is very large at small ones. The measured lattice spacing, of course, represents the position of equilibrium between these two forces. It is usual to express this repulsive term as a convergent infinite series and to determine the coefficients of the separate terms directly by comparison with the measured compressibilities (for if the potential function is known the theoretical compressibility can be written down immediately). This has been done, *e.g.*, by J. C. Slater,[48] whose work also confirms our assumption above that the attractive forces are purely electrostatic in nature. But the scope of the measurements, even over the largest possible range, is not sufficient to determine more than the first two coefficients in the expansion, so that extrapolation of the potential function beyond the experimental range becomes very hazardous. Several attempts[42] have been made to suggest forms of function which on theoretical grounds would permit of this extrapolation with more confidence.

Dielectric Properties of Crystals.—The theory of the dielectric properties of crystals and a discussion of the work on ice was summarised by P. Debye.[49] More recently J. Errera [50, 51, 52] and his school have investigated a number of substances, in many cases with special reference to the relation of the dielectric constant to the crystallographic direction. The work falls into two parts according as the crystals do or do not contain orientable permanent dipoles. The alkali and alkaline-earth halides illustrate the rule that the portion of the dielectric constant which may be attributed to relative displacement of the ions of opposite electric signs decreases with increasing size of anion for a given kation and also decreases with increasing size of kation for a given anion. The nitrates of lead, calcium, strontium, and barium follow the same rule, the case of lead, which has the same ionic radius as barium, showing the increase of ionic polarisation with increase of atomic number. The fluorides of iron, cobalt, and nickel have ionic polarisations which increase in this order, corresponding to the decrease in ionic size. The remarkable case of rutile and anatase, for which the dielectric constants are 114·0 and 48·0 respectively, has not received adequate explanation. The orthorhombic sulphates of strontium, barium, and lead show an unexpectedly high value of the dielectric constant along the *b*-axis. As for the nitrates, the ionic polarisation for the lead salt is much greater than for the barium and the strontium salt. The rhombohedral carbonates show the greatest ionic polarisation along the trigonal axis, whilst for the rhombic carbonates the differences along the crystallographic axes are much less marked. The platinocyanides of calcium, strontium, and barium show in each case the greatest dielectric constant perpendicular to the principal cleavage. Although they contain water of crystallisation, they do not show the dispersion with frequency characteristic of ice. The magnesium salt, containing seven instead of five molecules of water of crystallisation, does show this anomalous dispersion for the direction perpendicular to the good cleavage (001). Thus two molecules of water of crystallisation are differentiated from the others and are orientable when the field is applied in a particular direction.

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[45] *Z. physikal. Chem.*, 1933, **22**, 261; *A.*, 1001.

[46] "The Physics of High Pressures," and subsequent papers, especially in *Proc. Amer. Acad. Arts Sci.*

[47] *Physikal. Z.*, 1918, **19**, 529; Sherman, *Phil. Mag.*, 1932, **14**, 745.

[48] *Physical Rev.*, 1924, **23**, 488.

The investigation of the crystals containing permanent dipoles which may be oriented in the electric field has given results which suggest important applications in problems of crystal structure. As mentioned above, salts containing water of crystallisation sometimes show a dispersion of the dielectric constant both with frequency and with temperature similar to that observed in ice. It occurs in

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[49] "Polare Mölekeln," Leipzig, 1929.

[50] *Physikal. Z. Soviet Union*, 1933, **3**, 443.

[51] *Physikal. Z.*, 1933, **34**, 368; *A.*, 663.

[52] J. Errera and H. Brasseur, *Compt. rend.*, 1933, **197**, 480; *A.*, 1000.

$CuSO_4,5H_2O$ and $Na_2S_2O_3,5H_2O$ and appears to be associated with loosely bound water of crystallisation. Thus in gypsum and in most alums [52] there is no such anomalous dispersion. Rochelle salt has been extensively studied in connexion with its piezo-electric and dielectric characters. Errera has extended the frequency range of the investigation and found the same great increase in the dielectric constant at a particular frequency and over a restricted temperature interval of $-10°$ to $+25°$. The maximum dielectric constant recorded is 1300 for a field strength of 200 volts/cm. The electrical properties of mixed crystals from sodium potassium tartrate [53, 54] have also been studied. The application of X-ray diffraction to the study of the displacement of the ions in Rochelle salt [55] in an electric field marks an important advance. Another phenomenon [50] which may be important in the study of liquid crystals is the anomalous rapid rise in the dielectric constant of acetic acid and of p-azoxyanisole just at the moment of crystallisation. It occurs only for low frequencies. The tentative explanation put forward by the discoverer is that just on solidifying the liquid condenses into a large number of polar groups which in a field of low frequency can orientate themselves.

Electrical Breakdown in Crystals.—During the past three years a systematic study of the phenomena accompanying electrical breakdown in crystals has been made. To cause the discharge to pass through the crystal it is necessary to overcome the tendency of the discharge to pass round the edges of the specimen. This has been done by (Miss) L. Inge and A. Walther,[56] who used a point electrode resting on the crystal which in turn rested on a large plate. Under normal conditions of discharge, of duration greater than 10^{-7} sec., the crystal is destroyed, but by using special electrical circuits these authors were able to apply the potential for so short a time that the discharge did not strike right through the crystal. A. von Hippel [57] also succeeded in avoiding spurious effects by placing the crystal between two slightly rounded electrodes, filling the space between crystal and electrodes with specially prepared bees-wax, and mounting this apparatus in nitrogen at a pressure of about 100 atmospheres. The results obtained by the two methods are not always the same. For instance, for rock salt, Inge and Walther find that the discharge passes from the pointed electrode along [111] directions in the crystal, whereas Hippel finds that first [110] and then [111] are the

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[53] M. A. Ereméev, P. P. Kobeko, B. V. Kurtschatov, and I. V. Kurtschatov, *J. Exp. Theor. Physics Russia*, 1932, **2**, 102.

[54] B. V. Kurtschatov and M. A. Ereméev, *Physikal. Z. Soviet Union*, 1932, **1**, 140; *A.*, 1932, 560.

[55] H. Staub, *Physikal. Z.*, 1933, **34**, 292; *A.*, 447.

[56] *Z. Physik*, 1930, **64**, 830; *A.*, 1930, 1504; *Arch. Elektrotechnik*, 1929, **22**, 410.

[57] *Z. Physik*, 1931, **67**, 707; **68**, 309; 1932, **75**, 145; *A.*, 1931, 546; 1932, 565.

favoured directions. In the latter experiments the discharge always branches from the anode, whereas in Inge and Walther's work the branches grow from the point in each case, but much better when it is positive than when it is negative. The difference between these results is presumably due to the fact that in Hippel's apparatus the discharge begins in a fairly uniform field and only after the track has penetrated a certain distance into the crystal does the gradient at its end become very steep. In Inge and Walther's method the gradient at the beginning of the discharge, being that around the point, is very steep. For barytes, the favoured directions for the discharge are approximately [100], [101] and [011]; in calcite, two of the [$1\bar{1}1$] directions (which correspond to [111] in sodium chloride); in fluorite [100] and [111] occur according as the plates are cut parallel to (111) or (100); in beryl the discharge tracks run parallel to the hexad axis—a direction in which there are "holes" in the structure. Hippel has investigated the variation of the strength of the breakdown field in the alkali halide series and finds, after making allowance for small differences for different crystallographic directions, values which range from $\gg 2{\cdot}0 \times 10^6$ volts per cm. for lithium fluoride to $0{\cdot}50 \times 10^6$ volts per cm. for rubidium iodide. Parallel with this decrease in the breakdown field goes a change in the appearance of the tracks. For lithium fluoride they are sharp but become more diffuse as the ionic radii increase. Experiments on magnesium oxide indicate that the exchange of a doubly for a singly charged ion in the same structural type leads to a great increase in dielectric strength. Considerable difference of opinion existed between the investigators as to the mode of origin of the tracks, whether by acceleration of positive ions or of electrons. The total evidence appears to favour Hippel's view that the phenomenon is primarily due to electrons, accelerated towards the anode, acquiring sufficient energy to ionise by collision. The track of the electrons becomes conducting, and as it advances towards the cathode the potential gradient at its advancing end increases. Plastic deformation increases the dielectric strength, which would not be expected if ions were the conductors, since the cracks introduced by the deformation would provide easier paths for the ions than exist in the undeformed crystal. Other difficulties in accounting for the facts by an ionic discharge are that the time of the discharge is shorter than would be expected in this case, and that the breakdown potential is independent of the previous ion current. Hippel supposes that a slow-moving electron makes collisions with the atoms and loses energy to them in thermal agitation. As the velocity of the electron is increased, it will lose more energy per impact, corresponding to the greater number of acoustic, thermal, and infra-red characteristic frequencies to which it may lose energy.

If it has energy greater than the characteristic frequency of the lattice, *i.e.*, the " reststrahlen " frequency, it will begin to accumulate energy and bring about the discharge. This is borne out by the constancy (within 12%) for all the alkali halides of the ratio of the energy acquired by an electron in falling in the breakdown field through a length equal to the side of the unit cell to the quantum associated with the " reststrahlen " frequency. The correlation of the direction of the breakdown paths with the crystal structure is not yet clear, but it has been suggested with a certain amount of experimental justification that the discharge occurs in directions in which there are rows of neighbouring ions having the same sign of charge.

The Elastic and Plastic Properties of Crystals.—Elasticity. Several new methods of determining elastic moduli have been introduced.[58–63] In one of these[58] H-shaped masses were attached to the ends of the rod under test, which was supported by a long thin bifilar suspension. The outer limbs of the upper H were bar-magnets each of which was surrounded by coils of many turns in which currents were induced by the vibration of the magnets. These induced currents were amplified and the frequency was compared with a known frequency impressed on the same circuit. The bar was set into oscillation by a blow with a small hammer imparted to the end of one of the magnets. This mode of producing oscillation gave rise to both torsional and flexural vibrations, but these could be distinguished by observation of the sum and difference of the currents induced in the two coils. The elastic moduli were calculated from the vibration frequency and the dimensions of the rod. Another apparatus[59] for determining elastic moduli consisted of two identical gravity pendulums suspended from the top of the test plate which was clamped at the bottom. When one pendulum was started, the slight movement of its support caused the other pendulum to begin swinging. This process continued until the first had stopped swinging, its energy having been transferred to the second. The time between two successive stoppages of the same pendulum, together with the relevant dimensions of the apparatus, were sufficient data for calculating Young's modulus for the crystal plate. By using torsional instead of gravity pendulums, the rigidity modulus was found. The method devised originally by Quimby[62] has been adapted to measurements of elastic moduli by Zacharias.[63] A composite bar consisting of quartz cemented to the end of the bar under test was suspended by threads so as to vibrate freely. The quartz had been cut so that it could be set into longitudinal vibration on applying an alternating potential to its side faces. To find the unknown modulus for the crystal, it was necessary to know the frequency for which resonance occurred between the vibrations of the composite rod and the electrical circuit, the dimensions of the quartz and crystal, and the elastic constants of the quartz. Recent determinations of elastic constants include those of magnesium,[64, 65] quartz,[66, 67] gold–silver,[68] aluminium,[69] copper,[70] nickel,[63] and Rochelle salt.[61] The dynamical methods of determining the elastic moduli depend on the theory of torsional and flexural vibrations of a monocrystalline rod. This has been worked out by E. Goens,[71] using the fundamental work of Voigt. Although primarily concerned with piezo-electric characters, the book by P. Vigoureux [72] gives an excellent presentation of the theory and data of the elastic properties of quartz.

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[58] E. Goens, *Ann. Physik*, 1930, **4**, 733; *A.*, 1930, 764.

[59] P. le Rolland and P. Sorin, *Compt. rend.*, 1933, **196**, 536.

[60] E. Goens, *Ann. Physik*, 1933, **16**, 793.

[61] R. M. Davies, *Phil. Mag.*, 1933, **16**, 97; *A.*, 893.

[62] S. L. Quimby, *Physical Rev.*, 1925, **25**, 558.

[63] J. Zacharias, *ibid.*, 1933, **44**, 116; *A.*, 893.

Plasticity. Much has been written on the plastic deformation of metals, but it would not be profitable to attempt a review of this subject here. Among non-metallic substances, rock-salt has been most studied. Whilst there is good reason for investigating this substance on account of its simple crystal structure and the developed state of its lattice theory, yet generalisations are dangerous until the corresponding data are available for more substances. The experiments on the increase of the tensile strength of rock-salt on wetting, described originally by Joffé, have called forth many investigations.[73–83] Some of the results of these have verified the increase

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[64] P. W. Bridgman, *Proc. Amer. Acad. Arts Sci.*, 1932, **67**, 29; *A.*, 1932, 681.

[65] E. Goens and E. Schmid, *Naturwiss.*, 1931, **19**, 376; *A.*, 1931, 673.

[66] V. Fréedericksz and G. Michailov, *Z. Physik*, 1932, **76**, 328; *A.*, 1932, 799.

[67] R. de Mandrot, *Helv. Phys. Acta*, 1932, **5**, 362.

[68] H. Röhl, *Ann. Physik*, 1933, **16**, 887; *A.*, 561.

[69] E. Goens, *ibid.*, **17**, 233; *A.*, 768.

[70] K. Kimura, *Sci. Rep. Tôhoku Imp. Univ.*, 1933, **22**, 553.

[71] *Ann. Physik*, 1932, **15**, 455.

[72] "Quartz Resonators and Oscillators," London, 1931.

[73] A. Smekal, *Physikal. Z.*, 1931, **32**, 187; *A.*, 1931, 552.

[74] U. Heine, *Z. Physik*, 1931, **68**, 591; *A.*, 1931, 791.

[75] E. Rexer, *ibid.*, **72**, 613; *A.*, 1932, 13.

[76] G. F. Sperling, *ibid.*, 1932, **74**, 476; *A.*, 1932, 452.

[77] N. Seljakov, *ibid.*, 1932, **76**, 535; *A.*, 1932, 904.

[78] L. Piatti, *ibid.*, **77**, 401; *Nuovo Cim.*, 1932, **9**, 102; *A.*, 342.

[79] *Idem*, *ibid.*, p. 180.

[80] N. Seljakov, *Z. Krist.*, 1932, **83**, 426.

[81] K. H. Dommerich, *Z. Physik*, 1933, **80**, 242; *A.*, 342.

[82] L. Piatti, *Nuovo Cim.*, 1933, **10**, 43.

[83] N. N. Davidenkov and M. V. Klassen-Nekludova, *Physikal. Z. Soviet Union*, 1933, **4**, 25.

of tensile strength caused by wetting.[74–76] A rotation of some portions of the crystal relative to others through angles up to 30° is observed in the wet salt but not in the dry.[76] The distortion of the lattice makes it monoclinic near the surfaces along which gliding occurs.[73, 76] The crystals show a considerable increase in strength after previous plastic deformation, but this author finds that the elastic limit of previously undeformed and uniformly dissolved cleavage rods of rock-salt agrees within the error limit with that of dry natural crystals.[81] Measurement of the hardness of rock-salt by the damping method with the Kusnetzov pendulum [83] shows no difference in hardness between the dry and the previously wetted rock-salt. Further, the elastic limit of the rock-salt in water, determined in polarised light, is the same as that of the dry salt.

Investigations on dry rock-salt have been summarised by A. Smekal.[84] He concludes that the purest crystal prepared under the best conditions still has inhomogeneities which are responsible for the difference between the characters, in particular the breaking strength, of the actual and the theoretically ideal crystals. On applying stress to the crystal, glide planes develop from these inhomogeneities as soon as the stress exceeds the breaking or shearing stress for the ideal crystal. The crystal is no longer single but polycrystalline, and further deformation merely alters the number and mutual orientation of the individual grains. At a temperature somewhat below the melting point and for extensive deformation the polycrystal reaches a breaking strength close to that of the theoretical crystal, a fact which is explained as being due to the great disarrangement of the grains which prevents any further gliding, so that the real strength of the crystal is observed. The justification for this theory is based on extensive experiments. The strength of the pure crystal (99·995% pure) has been found at temperatures from 1·2° K. up to the melting point.[85–88] The strength is constant up to − 190°, decreases to + 40°, and then increases until near the melting point. The effect of known amounts of impurities has also been determined.[86, 89, 90] The complications arising from the plasticity have been almost overcome by working at low temperatures. The influence of impurities may be seen from the following example.[86] Rock-salt containing 0·045% of strontium chloride has, at room temperature, a tensile strength of 1000 g./mm.² as compared with 213 g./mm.^{2} for the pure substance. The increase of strength caused by the impurity decreases as the temperature is lowered, until at − 110° it is zero. On still further lowering of temperature, the impurity weakens the crystal until at − 190° and − 252° the same amount of impurity reduces the strength from 560 g./mm.^{2} to 135 g./mm.^{2} A. Smekal [84] concludes that the influence of impurities could certainly explain the difference between the ideal breaking stress (20,000—40,000 kg./cm.^{2}) and that of the best realisable crystal (60 kg./cm.^{2}). If an artificially coloured rock-salt crystal be deformed as far as possible, its absorption maximum moves towards the red (465 to 475 μ).[84] The corresponding change in excitation energy is 0·05 volt, and if this be interpreted as being the strain energy of the lattice at the coloured inhomogeneity, the corresponding stress is 16,000 kg./cm.^{2}. This value is close to that of the theoretical rock-salt crystal and the observation shows that the stress at the points where gliding occurs reaches nearly to the ideal breakdown stress. As the crystal is progressively deformed, irreversible double refraction [91, 92] first appears at a stress of about 5 kg./cm.^{2}. At the same stress, the photoconductivity begins to increase [93] and the ionic conductivity first begins to vary.[84] The very beginning of the process of deformation is therefore connected with an increase in the number of inhomogeneities and with the break-up of the single crystal. It is therefore improbable that ideal gliding ever occurs, and that even in metals, *e.g.*, zinc, where the gliding appears so simple, there is from the beginning of the deformation an irreversible increase in the number of faults in the lattice. The plastic properties of rock-salt at temperatures up to 600° have been investigated with special reference to annealing and increase of strength with plastic deformation.[88, 94–98] Since very small amounts of impurities greatly affect the mechanical properties of rock-salt, a method has been devised of observing them by means of an ultramicroscope. The number of ultramicroscopic particles can be correlated with the mechanical properties and ultra-violet absorption.[99, 1] The energy imparted to the crystal as a result of

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[84] *Physikal. Z.*, 1933, **34**, 633; *A.*, 1005.

[85] W. Burgsmüller, *Z. Physik*, 1933, **80**, 299; *A.*, 342.

[86] *Idem, ibid.*, **83**, 317.

[87] W. Burgsmüller and K. Steiner, *ibid.*, p. 321.

[88] W. Theile, *ibid.*, 1932, **75**, 763; *A.*, 1932, 683.

[89] A. Edner, *ibid.*, 1932, **73**, 623; *A.*, 1932, 219.

[90] H. Schönfeld, *ibid.*, 1932, **75**, 442.

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[91] I. W. Obreimov and L. W. Schubnikov, *Z. Physik*, 1927, **41**, 907.

[92] W. Schütze, *ibid.*, 1932, **76**, 135; *A.*, 1932, 799.

[93] H. J. Schröder, *ibid.*, p. 608; *A.*, 1932, 898.

[94] K. Przibram, *Sitzungsber. Akad. Wiss. Wien*, 1932, **141**, 63.

[95] *Idem*, *ibid.*, p. 645.

[96] E. Rexer, *Z. Physik*, 1932, **75**, 777.

[97] F. Rinne and W. Hofmann, *Z. Krist.*, 1932, **83**, 56.

[98] N. A. Brilliantov and I. W. Obreimov, *Physikal. Z. Soviet Union*, 1933, **3**, 83.

[99] R. Matthäi, *Z. Physik*, 1931, **68**, 85; *A.*, 1931, 563.

[1] E. Rexer, *Physikal. Z.*, 1931, **32**, 215.

deformation may, in the case of metals, be of a kind which cannot be detected by X-rays, *i.e.*, is not accounted for by the change in the lattice dimensions.[2] In one case it was shown that about 0·1% of the extension energy was retained by the strained lattice, whereas 15% of the energy was left in the crystal under some other form of strain. Measurements of the force and work necessary to produce cleavage in several crystals under various conditions have been made.[3–6] Two investigations on quartz [7, 8] have thrown light on its previously obscure plastic properties. The production of mechanical twins and their demonstration by etching is both striking and convincing. The breaking stress under compression is fifteen times smaller at the transition temperature, 573°, than at room temperature. The plastic properties of fluorspar,[9] calcite,[10] potassium halides,[92] mica [11] and the nature of the glide planes in a catholic selection of substances [12, 13] have also been studied.

Secondary Structure.—It has been generally assumed that an ideal lattice of the rock-salt type is stable. The calculations of the tensile strength based on this assumption lead, as was mentioned above, to a value several hundred times greater than that observed in the best crystals. This led F. Zwicky [14] to put forward the theory of "secondary structure" which is, briefly, that superimposed on the well-established lattice, known from X-ray diffraction, is another lattice on a scale such that its unit cell would have a side about 1 μ long. The planes of this lattice are supposed to contain more ions per unit area than parallel planes in the rest of the crystal. According to this picture, the crystal would, however pure and however carefully prepared, grow with a "block" structure. The weakness of the natural crystals is, according to this view, a necessary consequence of the nature of the secondary structure. This hypothesis has been used to explain many of the periodic or pseudo-periodic phenomena occurring in crystals and the existence of these periodicities, on a scale of about 1 μ, has been taken by Zwicky and others as support for the theory. Smekal has concluded that no such hypothesis is necessary to explain the weakness of the natural rock-salt crystal, the natural inhomogeneities both mechanical and chemical being the prime cause of the diminution of strength. If the hypotheses of secondary structure is unnecessary it remains to account for the large-scale periodicities. A short account of these follows.

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[2] V. Caglioti and G. Sachs, *Z. Physik*, 1932, **74**, 647; *A.*, 1932, 452.

[3] H. Tertsch, *Z. Krist.*, 1930, **74**, 476; *A.*, 1931, 422.

[4] *Idem, ibid.*, 1931, **78**, 53; *A.*, 1931, 1360.

[5] *Idem, ibid.*, 1932, **81**, 264; *A.*, 1932, 452.

[6] *Idem, ibid.*, p. 275; *A.*, 1932, 452.

[7] A. Schubnikov and K. Zinserling, *ibid.*, 1932, **83**, 243.

[8] K. Zinserling and A. Schubnikov, *ibid.*, 1933, **85**, 454.

[9] E. Rexer, *ibid.*, 1931, **78**, 251.

[10] O. Mügge, *ibid.*, 1932, **82**, 59.

[11] E. Orowan, *Z. Physik*, 1933, **82**, 235.

[12] O. Mügge, *Z. Krist.*, 1930, **75**, 32; *A.*, 1931, 415.

[13] *Idem, ibid.*, 1931, **76**, 359; *A.*, 1931, 550.

[14] *Helv. Phys. Acta*, 1930, **3**, 269; **3**, 466; **4**, 49; 1933, **6**, 210; *Physical Rev.*, 1932, **40**, 63; *A.*, 1932, 564.

The diffraction effects observed in crystals of potassium chlorate were thoroughly investigated by R. W. Wood,[15] and he concurred with Stokes in interpreting them by assuming periodic twinning. As many as 1000 planes, almost equidistant from one another, must occur in a single crystal in order to explain the narrowness of the spectral band reflected at a particular angle by the crystal. The natural (111) faces of perfect crystals of bismuth show fine striæ intersecting at 60°. A. Goetz [16] has attempted to show that the distances between the striæ are all simple multiples of about 1 μ by superposing a triangular network of lines on the observed pattern and adjusting the size of the triangles until each observed line coincided with a line of the net. The side of the smallest triangle so found is given as 1·4 ± 0·2 μ. The correspondence between net and striæ is not convincing, particularly as neighbouring lines are not always parallel and their distance apart is only a few times their width. Goetz has etched the (111) faces of bismuth crystals very carefully, and found that triangular pits are developed. He asserts that the sides of these triangles coincide with the lines of the net already fitted to the crystal in the previous observation. The published photographs do not give much support to this. Another line of research has been pursued by M. Straumanis.[17, 18] Crystals of cadmium and zinc were prepared by sublimation under carefully controlled conditions. The edges of the hexagonal plates so formed were bounded by heavily striated faces. A vertical section through the crystal showed a step-like formation at the edge, and he found that the heights of the steps were approximately whole multiples of 0·8 ± 0·1 μ. Zinc crystals also formed by sublimation were deformed so that gliding took place along the basal plane. The crystal after deformation appears, when viewed from the side, like a pack of cards pushed over to one side. The steps, however, are not bounded by vertical faces but by curved sloping faces, showing that gliding has occurred also on planes in between those usually denoted as slip-planes. The latter are 0·8 ± 0·1 μ apart, a distance equal to the height of the steps obtained when the crystal is grown by sublimation. It is difficult to judge from the photographs within what limits the separation of the glide planes is a whole multiple of 0·8 μ, but it is clear that the separation is often several times this distance. Thus, although the phenomenon of gliding may be associated with a lattice the planes of which are 0·8 μ apart, they are not all equivalent—a fact which distinguishes this type of lattice from that determined by *X*-ray analysis. On a scale about 100 times greater than that involved in the above experiments, periodic precipitation of cadmium between single crystals of zinc was observed by Straumanis.[19] Photographs show that the precipitations occur at intervals which are constant to within about 10% and vary according to the rate of crystallisation and the concentration of cadmium from about $\frac{1}{8}$ to $\frac{1}{3}$ mm. Investigations have also been made of the etching of various faces of zinc crystals by hydrochloric acid, and in many cases the etching has taken place along nearly parallel and equidistant lines. It is important to observe that the lines are sometimes not parallel, though the deviation from parallelism is small. In a paper[20] on the lattice-like inclusions of magnesium silicate in calcite from North Burgess, Ontario, are some photographs which show inclusions arranged parallel and, over a limited region, equidistant. The separation is of the order of 0·1 mm. When larger regions are considered it would be necessary, if a fundamental repeat distance were sought, to choose one not much larger than the width of the inclusions themselves. The inclusions were presumably deposited whilst the crystal was solid along the intersections of twin planes. The regularity of the spacing of the needles is thus an indication of the regular spacing of the twin planes.

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[15] "Physical Optics," 1911, p. 160.

[16] *Proc. Nat. Acad. Sci.*, 1930, **16**, 99; *A.*, 1930, 670.

[17] *Z. physikal. Chem.*, 1931, [*B*], **13**, 316; *A.*, 1931, 1115.

[18] *Z. Krist.*, 1932, **83**, 29; *A.*, 1932, 1080.

It has been suggested that the discrepancy between the wave-lengths of *X*-rays determined from crystals and from artificially ruled gratings is due to the secondary structure.[21] The planes of the secondary structure are supposed to be of greater density than the rest, and this would therefore cause a small error in the determination of wave-length. However, there is disagreement between various authors [22–24] as to whether there is any discrepancy between the wave-lengths obtained by the two methods. Some physical properties of bismuth crystals are different according as they are grown in or out of a magnetic field.[25, 26] No difference could be found between the spacing of the (111) and (1$\bar{1}$1) planes of crystals grown in, and of those grown out of, a magnetic field, indicating that the changes in physical properties were associated with the way in which the blocks of perfect crystal were assembled rather than with the properties of the blocks themselves.[27] Mention has already been made of the reported difference between the thermal expansion determined optically and by *X*-rays for bismuth. This result is interpreted as indicating that the portions of the crystal between the planes of the secondary structure expand uniformly up to the melting point, but that the planes of the secondary structure begin to break down at a temperature 35° lower.

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[19] *Z. anorg. Chem.*, 1929, **180**, 1.
[20] R. P. D. Gradham, *Min. Mag.*, 1918, **18**, 252.
[21] F. Zwicky, *Proc. Nat. Acad. Sci.*, 1930, **16**, 211; *A.*, 1930, 660.
[22] E. Bäcklin, *Physical Rev.*, 1932, **40**, 112.
[23] J. A. Bearden, *ibid.*, p. 471.
[24] Yuching Tu, *ibid.*, p. 662.

In attempting to form an opinion on the existence of the secondary structure from these periodic phenomena, it is important to bear in mind our ignorance of the exact nature and origin of the inhomogeneities which are so important in rock-salt. The other substances cited were probably not so pure as the rock-salt used by Smekal, and a rhythmic separation of the impurities might well give rise to the observed phenomena. A special theory is not required to explain the separation of cadmium from zinc on a macroscopic scale, and it seems unnecessary to introduce one when the scale is reduced a thousand-fold.

B. W. R.
W. A. W.

STRUCTURAL CRYSTALLOGRAPHY.

The methods of structure analysis have not been radically altered in the past two years, but they have acquired additional certainty and precision. The Weissenberg goniometer [1] has come more and more into use, and, together with other moving-film goniometers,[2] has made the indexing of reflexions and determination of space group a purely mechanical operation, so that mistakes on this score have practically disappeared. At the same time the use of integrating photometers [3] has made photographic intensity determination as accurate as ionisation spectrometer measurement, thus immensely extending the range of crystals available for com-

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[25] A. Goetz and M. F. Hasler, *Physical Rev.*, 1930, **36**, 1752; *A.*, 1931, 292.

[26] A. Goetz and A. B. Focke, *ibid.*, 1931, **37**, 1044; *A.*, 1931, 792.

[27] A. Goetz and R. C. Hergenrother, *ibid.*, 1932, **40**, 137; *A.*, 1932, 681.

[1] *Z. Physik*, 1924, **23**, 229; J. Böhm, *ibid.*, 1926, **39**, 557.

[2] H. Braekken, *Z. Krist.*, 1932, **81**, 309; *A.*, 1932, 449; E. Schiebold, *ibid.*, 1933, **86**, 370; E. Sauter, *ibid.*, 1933, **84**, 461; **85**, 156; *A.*, 451, 480; B. W. Robinson, *J. Sci. Instr.*, 1933, **10**, 165; *A.*, 689.

[3] *Idem*, *ibid.*, p. 233; *A.*, 1026.

plete analysis, especially for organic crystals, where the work of the Davy Faraday Laboratory (see below, p. 414) has been so outstanding. Fourier analysis, though still very laborious, has been undertaken in many cases, and it has become the recognised end of a structure determination to give, not only the atomic positions, interatomic distances, and angles, but some idea of the electronic density at different points in the cell. At the same time, methods of handling small crystals,[4] amorphous solids, fibres, and liquids have so improved that it may now be fairly claimed that there is no material, however minute in quantity or unpromising in appearance, that will not yield significant information on examination with *X*-ray or electron methods.

Quite apart from structure analysis, *X*-ray methods can be used for accurate quantitative analysis by measurement of intensities of diffraction : this has been used by M. E. Nahmias [5] to study the changes occurring in the production of porcelain from clay.[6] Of more general application have been the methods based on the precise measurements of spacing. Lattice dimensions can now be measured to one part in 100,000, and without undue difficulty to one in 10,000, particularly by a simple method, adaptable to any powder camera, developed by A. J. Bradley and A. H. Jay.[7] Dimensions thus obtained are highly characteristic for a pure substance. J. A. Bearden,[8] for instance, found for three samples of calcite from different localities spacings of 3·02805, 3·02807, and 3·02808 Å. at 20°. However, traces of substances in solid solution affect the spacings in a regular manner, and the variation can be used to determine the amount of the phase constituents. By quenching at different temperatures, or still better by the use of a high-temperature *X*-ray camera,[9] phase boundaries can thus be followed with an accuracy which, for the vertical lines of the equilibrium diagram, surpasses that of any other method.[10] Precision spacing measurements have also been used for measurement of true thermal expansion of crystals in different directions,[11] as they can be used where interferometer methods are out of the question. Extension of *X*-ray methods to low temperatures have also been notably improved, especially through the work of M. Ruhemann.[12]

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[4] O. Kratky and K. Eckling, *Z. physikal. Chem.*, 1932, [*B*], **19**, 278; *A.*, 139.

[5] *Z. Krist.*, 1932, **83**, 329; *A.*, 44; *ibid.*, 1933, **85**, 319.

[6] *Ibid.*, 1933, **85**, 355; *A.*, 892; A. J. Bradley and A. L. Roussin, *Trans. Ceramic Soc.*, 1932, **31**, 422.

[7] *Proc. Physical Soc.*, 1932, **44**, 563; 1933, **45**, 507; *A.*, 1932, 1078; 1933, 891; (Miss) H. D. Megaw, *Phil. Mag.*, 1932, [vii], **12**, 130; *A.*, 1932, 800; cf. G. Sachs and J. Weerts, *Z. Physik*, 1930, **60**, 481; **64**, 344.

[8] *Physical Rev.*, 1931, [ii], **38**, 2089; *A.*, 1932, 217.

[9] A. H. Jay, *Z. Krist.*, 1933, **86**, 106; *A.*, 1026; *Proc. Physical Soc.*, 1933 **45**, 635.

[10] E. A. Owen and L. Pickup, *Proc. Roy. Soc.*, 1932, [*A*], **137**, 397; *A.*, 1932, 990; 1933, [*A*], **139**, 526; *A.*, 454; A. Westgren, *Assoc. Int. Essai Mat.*, 1932, **1**, 484; *A.*, 1007.

CRYSTAL CHEMISTRY.

Daltonian and Berthollide Compounds.

Possibly the most interesting development of crystal chemistry is that centring round the regular and irregular structure of compounds and solid solutions. From this field, evidence has been gradually accumulating which goes far towards changing our ideas on the laws of chemical composition. These laws, in particular Dalton's laws of constant and multiple proportions, were founded on the study of simple molecular compounds, hydrogen, oxygen, nitrogen, water, carbon dioxide, etc., and binary ionic compounds, such as sodium chloride and calcium carbonate. Here these laws hold in full rigidity, but there was something in Berthollet's view that they should not be extended to the whole of chemistry. In fact, it is only in molecular chemistry—which includes organic chemistry—that they are strictly true. In ionic chemistry they break down for the simplest ternary systems, as mixed oxide and mixed halide systems show, and for the chemistry of ores and metals even the conception of valency breaks down completely, and attempts to apply it only lead to unwieldy or incorrect formulæ.

The validity of constant composition and valency rules depends, we see now, either on definite directed electron-sharing bonds, or on the necessary equality of positive and negative ionic charges. The first is true only of molecules or molecule ions $(NO_3)^-$,$(CH_3COO)^-$, the second only leads to simple laws if all the ions of each sign are of the same kind. Apart from these cases, regularity may arise from the conditions of geometrical packing in crystals. Here it is not so much a question of bonds or charges, but of the size and shape of the units concerned, atoms, ions, molecule ions, or molecules. If the sizes of the various components are very different and the structure well fitted together, compounds result apparently of the true Daltonian type. Such compounds are NaK, the alums, or the molecular compounds of organic chemistry. They differ, however, from true chemical compounds by having no existence apart from the crystalline state.

If, however, the different units from which the crystal is built only differ slightly in size and shape, they may come to occupy indifferently the same positions. The simplest case of this kind is that of normal solid solution, as of silver and gold or the mixed crystal NaCl, KBr, and NaBr which may be written (NaK)(ClBr).

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[11] (Miss) H. D. Megaw, *Proc. Roy. Soc.*, 1933, [*A*], **142**, 198; A. H. Jay, *ibid.*, p. 237.

[12] *Z. Physik*, 1932, **76**, 368; J. A. Santos and J. West, *J. Sci. Instr.*, 1933, **10**, 219; *A.*, 925.

That size, and not charge or chemical character, is the preponderating factor, is shown by the work of E. Posnjak and T. F. W. Barth [13] in the case of lithium ferrite $LiFeO_2$, which has the rock-salt structure with Li^+ radius 0·78 Å. or Fe^{3+} radius 0·67 Å. occupying indifferently the cation positions. A more complicated case is presented by the spinels discussed in the last report (1931, **28**, 299). Barth's theory of interchangeability of ions, which he calls "variate atomic equipoints," has been established [14] for the spinels $MgFe_2O_4$, $MgGa_2O_4$, $MgIn_2O_4$, $TiMg_2O_4$, $TiFe_2O_4$, and $SnZn_2O_4$, but it does not hold for the aluminates of manganese, iron, cobalt, nickel, and zinc, and probably not for the typical spinel $MgAl_2O_4$. This conclusion has been confirmed by F. Machatschki: [15] the previous differences had arisen because the observers were working on different compounds. The ion equivalence is not confined to cations. E. Kordes [16] has prepared spinels of the type $(Mg,Li)Al_2(O,F)_4$. The presence of this extreme form of ion equivalence is, of course, connected with the high crystallising temperature—in the region of 1000°—of these crystals. That this, however, is not a necessary condition is shown by the appearance of the same phenomenon in molecular crystals. S. B. Hendricks [17] has shown that the crystals of *p*-chlorobromobenzene and an equimolar mixture of *p*-dichloro- and -dibromo-benzene are indistinguishable by *X*-ray methods, the molecule of the former possessing a statistical centre of symmetry showing that the intermolecular forces do not in this case distinguish between chlorine and bromine. The clearest cases of the conditions for interchangeable atoms are furnished by metals. Nearly all metals mix in the liquid state, and in the solid not only do similar metals, such as tungsten and molybdenum or antimony and bismuth, form mixed crystals in all compositions, but the face-centred metals γ-Mn, γ-Fe, β-Co, Ni, Cu, Rh, Pd, Ag, Ir, Pt, Au, all form solid solutions in each other, and in most cases these are unlimited. (Silver is somewhat exceptional, see p. 387.) In such a mixed crystal the atomic positions are rigidly fixed—in this case to the corners and face centres of a cube—but any kind of atom can occupy any place. In all cases this is the state of affairs just below the melting point, but in some a further regularity appears on slow cooling. For instance, in a mixture of the composition of Cu_3Au between 390° and the melting point at 960° all the atoms occupy indifferently the points of a face-centred lattice, but below 390° the gold atoms occupy the cube corners while the copper occupy the cube face centres. Such structures are very frequent among metals and have been called "überstrukturen," not very happily translated as "superstructures." Alloys with superstructures differ sharply from solid solutions in their mechanical, magnetic, and electric properties,[18] which resemble those of pure metals : but this is merely an effect of regularity, and they should not be considered as compounds unless we carefully distinguish between chemical compounds and crystal compounds. Our knowledge of them has been greatly extended by the detailed quantitative study of the iron–aluminium system by A. J. Bradley and A. H. Jay.[19] Pure iron and FeAl both have atoms arranged in cubic body-centred lattices : simply in iron, and with the centres occupied by Al atoms in FeAl (cæsium chloride structure). The intermediate alloys quenched from higher temperatures showed up to 25 atomic % of aluminium an irregular solid solution of aluminium in iron, between 25 and 50% aluminium an irregular solid solution of iron in FeAl, *i.e.*, with all the aluminium atoms not replaced by iron still in the cube-centre positions. In annealed specimens a further regular superstructure appeared in the composition 25% aluminium. This FeAl structure is also body centred but with a doubled cell of 16 atoms, and with iron atoms regularly disposed in half the centres of the eight small cubes making up the unit cell. For compositions between 18 and 40% aluminium this structure persists, but *X*-ray intensities show that replacement of iron or aluminium atoms takes place in a complex but statistically orderly way, tending to approximate to the simple Fe–Al or FeAl–Fe solid solutions.

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[13] *Physical Rev.*, 1931, [ii], **38**, 2234; *A.*, 1932, 217.

[14] T. F. W. Barth and E. Posnjak, *Z. Krist.*, 1932, **82**, 325; *A.*, 1932, 830.

[15] *Ibid.*, p. 348; *A.*, 1932, 830; S. Holgersson, *Z. anorg. Chem.*, 1932, **204**, 378, 382; *A.*, 1932, 481, 485.

[16] *Fortschr. Min., Krist. Petr.*, 1932, **17**, 432; *A.*, 1020.

[17] *Z. Krist.*, 1932, **84**, 85; *A.*, 216.

It is clear that in such cases we have to do with a phenomenon analogous to the melting of a crystal, referring, not to change between the regularity of atomic positions in a crystal and their irregularity in a liquid, but to the regular and irregular arrangements of atoms inside a given crystal structure. Such regular arrangement must have a slightly lower potential energy, and melts sharply with a correspondingly small latent heat of mixing of the atomic species. The melting point is depressed by addition of either constituent, as is that of a true compound. Undercooling, however, is easy, because the transformation requires interchange of atomic places; thus slow diffusion hinders the formation of superstructures. At low temperatures the irregular solid solution is in the same state, as far as position of specific atoms, as a glass; it is not in equilibrium but cannot acquire it. The quantitative thermodynamic study of such systems has been carried out by W. L. Bragg,[20] who has been able to show why the more complicated forms of superstructure such as Fe–Al cannot exist. In this connexion, it is worth recalling the recent studies in diffusion in the crystalline state, particularly by G. von Hevesy and his school,[21] but also by a great number of other authors.[22] There is no space here for an adequate discussion, but it may be pointed out that the diffusion rate D is given by $Qa^2/Nh \,.\, e^{-Q/RT}$, where N is Loschmidt's number, h Planck's constant, a is the shortest distance between exchangeable atoms, and Q is the characteristic heat of atom interchange of the substance; Q varies from 80 kg.-cal. per molecule for tungsten–molybdenum to 2·2 kg.-cal. for silver in silver iodide, and is itself a function of the characteristic temperature, or more simply, of the melting point of the substance $= 3b^2RT_S$, where b does not vary much from 2.

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[18] U. Dehlinger and R. Glocker, *Ann. Physik*, 1933, [v], **16**, 100; *A.*, 338; R. Glocker, *ibid.*, 1932, [v], **14**, 40; *A.*, 1932, 907.

[19] Iron and Steel Inst., May 1932; *A.*, 1932, 567; *Proc. Roy. Soc.*, 1932, [*A*], **136**, 210; *A.*, 1932, 685; K. Schäfer, *Naturwiss.*, 1933, **21**, 207; *A.*, 455.

In ionic compounds the anion diffusion is not much affected by the nature of the cation, but the converse does not hold. The velocity of diffusion of silver is least in the fluoride, increases to a maximum for the iodide and sulphide, and then falls to low values for the metallic AgSb, AgSn, AgAu. The effect of crystal distortion or fine grain size raises the diffusion constant in some cases by as much as 40 times, but does not alter the interchange energy.

The types of non-Daltonian compound that have been discussed can all be brought into line by abandoning an absolute effective distinction between atoms or ions of different elementary species, and treating them as substitutional mixed crystals. They can be formulated in a Daltonian manner by such expressions as $(Na_xK_{1-x})(Cl_yBr_{1-y})$ or $(Fe_{1-x}Al_x)_3(Al_{1-y}Fe_y)$, where x and y are no longer whole numbers, and where no particular value of x and y gives a compound sharply different from neighbouring values.

There are, however, two other forms of crystalline phase which strain the definitions and laws still further. The first of these is the interstitial compounds discussed in previous reports. The metals of the transition groups can, without changing their structure, admit small atoms such as hydrogen, boron, carbon, or nitrogen into the interstices between them, and these can exist either statistically distributed or in definite positions. These may be called *additional* solid solutions or *additional* crystal compounds respectively, and may be formulated $[Fe]N_x$ or $[Pd]H_{1/2}$. Another non-Daltonian type is that called by Hägg *subtraction* solid solution or compound, and has been studied particularly in the systems Fe–S [23] and Fe–Se,[24] and also in Fe–O studied by E. R. Jette and F. Foote.[25] The structures found are for FeO the simple sodium chloride structure, for FeS the NiAs structure, for FeSe the lead oxide structure at high and NiAs at low temperatures. In each case, however, a range of solid solution on the iron-poor side exists, and in fact the stoicheiometric compound FeO or FeS cannot be formed at all, in spite of the assurance of elementary chemical text books! The lattice shrinks as the iron content is reduced, which is consistent with the theory that it consists of an ideal lattice FeO, FeS, or FeSe, with an increasing number of iron atoms removed, leaving spaces which are partially filled by adjustments of the other atoms. Such *subtraction* solid solutions may be formulated $(Fe''Fe''')_{1-x}O$, etc. They may be expected in metallic compounds, where, owing to great difference of atomic type, substitution cannot take place, and in ionic compounds where the cation valency can vary. Subtraction compounds may exist as well as subtraction solid solutions: the γ structure of Cu_5Zn_8, Cu_9Al_4, etc., can be derived by dropping two positions from a three-fold body-centred structure of 54 atoms. Another example is the C-sesquioxide type of Mn_2O_3. This is a subtraction compound derived from a two-fold fluorite structure, in which one out of every four anions is dropped out, with consequent slight displacements of all the ions.

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[20] Private communication.

[21] *Z. Elektrochem.*, 1933 [*B*], 490; *A.*, 1000; *Naturwiss.*, 1933, **21**, 357; *A.*, 669.

[22] E. Owen and L. Pickup, *Nature*, 1932, **130**, 201; *A.*, 1932, 989; C. Matano, *Mem. Coll. Sci. Kyoto*, 1932, [*A*], **15**, 167, 351; *A.*, 1932, 907; 1933, 218; N. Ageev and M. Zamotorin, *Ann. Inst. Polytech. Leningrad*, Sect. Math. Phys. Sci., 1928, **31**, 15; *A.*, 1932, 15; W. Jost, *Z. physikal. Chem.*, 1933, [*B*], **21**, 158; *A.*, 561.

The necessity of considering these non-Daltonian or Berthollide compounds (a term first introduced by Kurnakow) [26] in relation to the ordinary conceptions and notations of chemistry is becoming increasingly urgent, as most metallic and sub-metallic (sulphide) systems are essentially of this type, as well as many ionic and molecular compounds. A. Öhman,[27] who has discussed this question from a structural and thermodynamic point of view, proposes to distinguish them by the use of non-integral suffixes instead of the integral ones of Daltonian compounds : for instance, for ε-brass he would write $\varepsilon\mathrm{Zn}_{0\cdot78}^{0\cdot89}\mathrm{Cu}_{0\cdot22}^{0\cdot11}$ expressing merely the ranges of composition. A more informative symbolism would refer to the number of interchangeable places in a crystal cell, extra places being indicated by +, empty places by —, but it is time the whole matter was taken up by an authoritative committee.

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[23] *Nature*, 1933, **131**, 167; *A.*, 342.

[24] R. Juza and W. Biltz, *Z. anorg. Chem.*, 1932, **205**, 273; *A.*, 1932, 563; G. Hägg and A. L. Kindström, *Z. physikal. Chem.*, 1933, [*B*], **22**, 453; *A.*, 1111.

[25] *J. Chem. Physics*, 1933, **1**, 29; *A.*, 214.

[26] *Z. anorg. Chem.*, 1914, **88**, 109.

[27] *Z. physikal. Chem.*, 1933, [*A*], **165**, 65.

Transformation and Segregation in the Solid State.

Closely related to the question of mixed crystals and solid solution is that of the actual mechanism of separation of a homogeneous crystal phase into two or more others. Recent work, particularly that of G. Sachs,[28] R. F. Mehl,[29] D. W. Smith,[30] M. L. Fuller,[31] and H. Hanemann,[32] has shown that when an ore metal phase separates on annealing into two, the separation takes place along certain lines or planes of the original crystal, giving rise to the Widmanstätten structure first observed in meteoric iron. In general, it is possible to show crystallographic reasons for the mutual arrangement on the interface between the new phases, the general principle being to minimise the amount of atomic interchange necessary. This phenomenon is by no means confined to metals : it lies at the back of most of the pseudomorphism, parallel growths, mimetic and polysynthetic twinning that occurs in natural minerals. The process has been experimentally studied in many oxide and hydroxide systems. W. Büssem and F. Köberich[33] have shown that when hexagonal brucite, $\mathrm{Mg(OH)_2}$, dehydrates to cubic periclase, MgO, the latter is oriented with its trigonal axis parallel to the original hexagonal axis. As, however, the corresponding planes are not quite identical, the periclase grows in a strained double refracting form which does not become isotropic till heated to 1150°. Similar observations have been made by M. Deflandre[34] and H. Schwiersch[35] on the transformation of diaspore AlO(OH) into corundum $\mathrm{Al_2O_3}$. These reactions are essentially similar to the polymerisation of organic molecules in the solid to be discussed later (p. 425).

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[28] *Z. Metallk.*, 1932, **24**, 241; *A.*, 1932, 1196.

[29] R. F. Mehl and C. S. Barrett, *Amer. Inst. Min. Met. Eng.* (Inst. Met. Div.), 1931, **93**, 78; R. F. Mehl and O. T. Muzhe, *ibid.*, p. 123; R. F. Mehl, C. S. Barrett, and F. N. Rhines, *ibid.*, 1932, **99**, 203; *A.*, 1932, 685.

[30] C. H. Mathewson and D. W. Smith, *ibid.*, 1932, **99**, 264.

[31] M. L. Fuller and J. L. Rodda, *ibid.* (Preprint), 1933; *A.*, 454.

[32] H. Hanemann and O. Schröder, *Z. Metallk.*, 1931, **23**, 271; *A.*, 1932, 220.

[33] *Z. physikal. Chem.*, 1932, [*B*], **17**, 310; *A.*, 1932, 811.

[34] *Bull. Soc. franç. Min.*, 1932, **55**, 140; *A.*, 1107.

[35] *Chem. Erde*, 1933, **8**, 252; *A.*, 1020.

Crystal Topology.

The reduction of the multiple observed crystal types to some common order based on topological relations between atoms and groups is becoming an urgent question, because crystal chemistry is largely unintelligible owing to its not being systematised. P. Niggli and his school[36] continue their work in this field, but their treatment is too formal as yet to have acquired many followers. However, the work of F. Laves[37] on the classification of the silicates indicates that the method has possibilities.

CRYSTAL STRUCTURE.

The number of papers on crystal structure in the last two years is still greater than ever before, and it has become quite impossible in the scale of these reports even to mention all the new structures described. The principle of selection has been to introduce only such investigations as break new ground, or those of wider chemical interest. The main lines of classification remain unchanged—Metallic, Sub-metallic, Ionic, and Molecular.

Metallic.

There has been great activity in the field of fundamental theory of metals, particularly of their electrical and magnetic properties, but most of this falls outside the scope of a chemical report. The work of U. Dehlinger,[38] however, is of peculiar systematic interest. He points out that the properties of metals depend on the one hand on the number of free electrons, and on the other, on the interaction between the remaining ionic cores. This interaction, which is practically nil for the alkali metals, reaches a maximum in the transition and coinage metals, where it is the determining factor for metallic properties. In particular, he links the colours of copper, silver, and gold to the instability (multivalence) of copper and gold, compared to the peculiarly stable alkali-like ion of silver. In metals of this type, miscibility in liquid and solid depends far more on the specific nature of the core than on atomic radius. Silver, for instance, though it has almost exactly the same atomic radius as gold, is far less miscible in the liquid or solid state with iron, cobalt, copper, etc. Electrons in metals can fulfil three functions. They can be free, belonging to the lattice as a whole; if the number of such electrons differs from the number of atoms a β-, γ-, or ε-structure results; or the electrons can belong predominantly to atom pairs, as in gallium, tin, bismuth, and B-group metals in general; or they may be bound to the cores, as in mercury, thallium, and lead, which function in the metallic state mainly as Hg, $Tl^{\cdot}$, and $Pb^{\cdot\cdot}$ (cf. this vol., p. 120). In general, atoms in compounds will not have the same charge as in the element. $Fe^{\cdot\cdot}$ in iron becomes Fe in iron–zinc alloys, as shown by the alloy type and magnetic measurements. There can be resonance between different possible states, as in the body-centred compound $[Cu^{++}Pd^{+}{}_{3-}]\rightleftharpoons[Cu^{+}Pd^{++}{}_{3-}]$, which thus has the required electron : atom ratio 3 : 2. We are clearly at the beginning of a theoretical metal chemistry of great complexity and interest. Its difficulty can be judged by the fact that the Hume-Rothery rules, which are more and more recognised as the empirical basis of metal chemistry, have not as yet been satisfactorily explained, though many attempts have been made, notably by U. Dehlinger,[38] H. Perlitz,[39] and Laves.[40] W. Hume-Rothery himself[41] has shown, by a study of the alloys of copper with B-group metals, that the position of the liquidus and solidus curve is determined by the electron and not by the atom content of the solid solution.

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[36] *Z. Krist.*, 1932, **83**, 111; *A.*, 1932, 986; *ibid.*, 1933, **86**, 121; *A.*, 1001; P. Niggli and W. Nowacki, *ibid.*, p. 65; *A.*, 1001; W. Nowacki, *ibid.*, 1932, **82**, 355; *A.*, 1932, 796; *idem*, *ibid.*, **83**, 97; *A.*, 1932, 986; H. Heesch, *ibid.*, 1933, **84**, 399; *A.*, 450; R. Reinicke, *ibid.*, 1932, **82**, 394, 419; *A.*, 1932, 796.

[37] *Ibid.*, p. 1; *A.*, 1932, 682; H. Heesch and F. Laves, *ibid.*, 1933, **85**, 443.

[38] *Z. Elektrochem.*, 1932, **38**, 148; *A.*, 1932, 452; *Metallwirt.*, 1932, **11**, 223; *A.*, 1932, 1193; *Z. physikal. Chem.*, 1933, [*B*], **22**, 45; *A.*, 881; *Naturwiss.*, 1933, **21**, 607; *A.*, 1005.

As already mentioned, high precision methods have been much applied recently, particularly to pure metals. Separate references will not be given, as the measurements up to the middle of 1933 have been collected by M. Neuburger.[42] Our knowledge of at least one form of structure of the metallic elements is now nearly complete; we lack knowledge only of scandium, masurium, ten of the rare-earth metals, radium, actinium, and protoactinium.

Transition Metals and Their Interstitial Compounds.—Further work on structures of transition metals at different temperatures has shown that the allotropy of the type of iron is the rule rather than the exception. Besides the regular, face-centred cubic, body-centred cubic, and hexagonal close-packed, which seem to be the normal forms at high temperatures, several much more complicated structures have been found, often formed by electrolytic deposition. These stable low-temperature forms are clearly difficult to get from the melt, owing to slow diffusion, and many transition metals are probably only known in their simple metastable forms. The particular structures, though complicated, are of special stability, as shown by their appearance in more than one metal, as the 58 atom per cell structure common to γ-Cr[43] and α-Mn, the 20 atom per cell structure of β-Mn found also in Cu_5Si, and the 8 atom per cell α-W[44] structure found also in Cr_3Si.[45] The last structure is one of some interest. A cubic cell of side 5·03 Å. for tungsten and 4·55 Å. for Cr_3Si contains two atoms at the corners and body centre, and six others in pairs on each face with co-ordinates of the type $0,\frac{1}{2},\frac{1}{4}$, $0,\frac{1}{2},\frac{3}{4}$. This gives a pseudo-icosahedral 12-fold co-ordination of the second type of atom (chromium) round the first (silicon), which is actually closer than that of normal cub-octahedral close packing.

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[39] *Acta Comm. Univ. Tartu.*, 1932, No. 24, 3; *A.*, 118.

[40] *Nach. Ges. Wiss. Göttingen*, Math.-phys. Kl., 1932, 519; *A.*, 1932, 1232.

[41] Private communication.

[42] *Z. Krist.*, 1933, **86**, 395.

The mechanism of allotropy has been studied in detail by U. Dehlinger[46] in the case of cobalt. The transformation from cubic hexagonal close packing takes place reversibly in single crystals. A similar transformation from cubic to tetragonal has been observed by L. Graf[47] to occur for the crystal compound AuCu. Much work has been done on the solid solution and superstructures among the transition metals : references only can be given.[48]

Great advances have been made in the study of interstitial compounds. K. Becker[49] has given an interesting summary of our knowledge of their physical properties. Most of them are exceedingly stable at high temperatures—vanadium carbide melts above 4000°—and are also extremely hard, approaching if not exceeding diamond. More work[50] has been done on the characteristic transformations of steel, which are typical examples of Widmanstätten structure (see above, p. 386). A. Westgren and his school have examined the more complex carbide, boride, and silicide systems. In the carbides, including high-speed steel carbides, the phases studied in order of increasing carbon content were the following :—

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[43] K. Sasaki and G. Sekito, *Trans. Amer. Electrochem. Soc.*, 1931, **59,** 437.

[44] M. C. Neuburger, *Z. Krist.*, 1933, **85,** 232; *A.*, 665; H. Hartmann, F. Ebert, and O. Breitschneider, *ibid.*, p. 232.

[45] See ref. 57.

[46] U. Dehlinger, E. Osswald, and H. Bumm, *Z. Metallk.*, 1933, **25,** 62; *A.*, 665.

[47] L. Graf, *ibid.*, 1932, **24,** 248; *A.*, 1932, 1196.

[48] F. M. Jaeger and E. Rosenbohm, *Proc. K. Akad. Wetensch. Amsterdam*, 1931, **34,** 808; *A.*, 1932, 14; W. Stenzel and J. Weerts, Siebert Festschr., 1931, 288; *A.*, 1932, 221; S. Kaya and A. Kussmann, *Z. Physik*, 1931, **72,** 293; *A.*, 1932, 15; P. Wiest, *ibid.*, 1932, **74,** 225; *A.*, 1932, 330; 1933, **81,** 121; *A.*, 450; H. J. Seeman, *ibid.*, **84,** 557; *A.*, 1000; G. D. Preston, *Phil. Mag.*, 1932, [vii], **13,** 419; *A.*, 1932, 221; (Miss) H. D. Megaw, *ibid.*, **14,** 130; *A.*, 1932, 800; R. W. Drier and H. L. Walker, *ibid.*, 1933, [vii], **16,** 294; *A.*, 895; H. J. Seeman, *Z. Metallk.*, 1932, **24,** 299; *A.*, 344; O. E. Zvjagintsev and B. K. Brunovski, *Z. Krist.*, 1932, **83,** 172; *A.*, 1932, 1107; A. Claassen and W. G. Burgers, *ibid.*, 1933, **86,** 100; *A.*, 1003; M. Le Blanc and G. Wehner, *Ann. Physik*, 1932, [v], **14,** 481; *A.*, 1932, 989; J. O. Linde, *ibid.*, **15,** 249; *A.*, 115; M. Le Blanc and W. Erler, *ibid.*, 1933, [v], **16,** 321; *A.*, 455; H. Röhl, *ibid.*, **18,** 155; *A.*, 1110; (Miss) M. L. V. Gayler, Iron and Steel Inst., 1933, Sept.; *A.*, 1008; W. Köster and W. Schmidt, *Arch. Eisenhüttenw.*, 1933–34, **7,** 121; *A.*, 1007; E. Schiedt, *Z. anorg. Chem.*, 1933, **212,** 415; *A.*, 773.

[49] *Physikal. Z.*, 1933, **34,** 185; *A.*, 343.

(1) Cubic Fe_3W_3C,[51] 96 metal atoms per cell. This is really a double interstitial structure, being based on a tungsten carbide framework held together by iron atoms. Isomorphous with this were Fe_4W_2C, Co_3W_3C, Ni_3W_3C, and Fe_3Mo_3C.

(2) Cubic $Cr_{23}C_6$,[52] 92 metal atoms per cell. This complex structure is built from cubes and cuboctahedra of metal atoms at an average distance of 2·5 Å. apart. Isomorphous with it are $Mn_{23}C_6$, $Fe_{21}W_2C_6$, $Fe_{21}Mo_2C_6$, and $Cr_{21}W_2C_6$.

(3) Orthorhombic Fe_3C. This is the familiar cementite structure. Westgren[53] has shown that the structures previously put forward for this (*Ann. Reports*, 1931, **28**, 294) are incorrect, in that the carbon atoms should be placed as in tungsten carbide and other carbides inside a trigonal prism, height and side 2·66 Å. Isomorphous with it are Mn_3C and $(MnFe)_3C$ (spiegeleisen).

(4) Hexagonal Ni_3C.[54] This somewhat unstable compound seems to be of Hägg's 12*b*, 6 type (see *ibid.*, p. 293).

(5) Trigonal Cr_7C_3 and Mn_7C_3. This has not been further studied and may have a more complicated formula.

(6) Hexagonal V_2C and Mo_2C, etc., of Hägg's 12*b*, 6 type.

(7) Rhombic Cr_3C_2.[55] This is the most interesting of the new structures. The cell is 11·5 × 5·5 × 2·8 Å., space group $D_{2h}^{16} - Pbnm$. All atoms lie in symmetry planes. The carbon atoms are placed at the centres of a distorted trigonal prism of chromium atoms, and form long zig-zag chains parallel to the diad screw axis *c*, the C–C distance being 1·64 Å. Here we have no longer a true interstitial compound, but one between chromium and dehydrogenated paraffin chains.

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[50] K. Honda and Z. Nishiyama, *Sci. Rep. Tôhoku Imp. Univ.*, 1932, **21**, 299; *A.*, 12; H. J. Wiester, *Z. Metallk.*, 1932, **24**, 276; *A.*, 119; H. Hanemann, *Arch. Eisenhüttenw.*, 1931–32, **5**, 621, 625; *A.*, 1932, 796, 797.

[51] *Jernk. Ann.*, 1933, 1–12, 14.

[52] *Ibid.*, pp. 501, 1215, 1217.

[53] *Ibid.*, 1932, 457.

[54] *Z. physikal. Chem.*, 1933, [*B*], **20**, 361; *A.*, 558.

[55] *Svensk Kem. Tidskr.*, 1933, **45**, 141; *A.*, 1003.

(8) Hexagonal WC, MoC, of Hägg's 8*b*, 6 type. Here again each carbon atom is at the centre of a trigonal prism of tungsten atoms.

The structures of the borides of iron, cobalt, and nickel have been studied by T. Bjurström :[56] the most interesting is that of FeB, in which, as in Cr_3C_2, the non-metal atoms form a zig-zag chain with a B–B distance of 1·78 Å. The average radius of the boron atom in these compounds is 0·93 Å. The silicides of chromium, manganese, cobalt, and nickel have been studied by B. Boren.[57] The most interesting is that of Cr_3Si, already mentioned. It is now well established that the hydrogen dissolved in palladium exists in the form of protons, as the heat of solution exceeds by about 20 kg.-cals. the heat of dissociation of molecular hydrogen. The nature of the solutions and their conductivities have been studied by F. Krüger and G. Gehm,[58] A. Coehn and K. Sperling,[59] and G. Rosenhall.[60] The conductivity is partially ionic, but the protons only carry a small fraction of an electronic charge, and must consequently be surrounded in the metal by an electronic cloud nearly neutralising them. This property of dissociating hydrogen molecules is shown to a less degree by nickel, and even less by other metals of the eighth group and copper. It is clearly a necessary condition for hydrogenating catalysis, but the catalytic efficiency falls off as the heat of combination with hydrogen increases; hence nickel is a better hydrogenator than palladium.

Electron Compounds.—The compounds between transitional and B (A) group metals obey Hume-Rothery's rules, and may appropriately be called electron compounds, as their crystal structure depends in the main merely on the ratio of electrons to the atoms they contain (see above, p. 388). Nearly fifty papers have in the past two years been devoted to *X*-ray work on these compounds : it is only possible to mention a small selection.

The range of alloy system investigated has been much increased from the system TiAl [61] to AgLi. In the latter system H. Perlitz [62] has shown that a true γ-phase exists between 76·3 and 80·2 atoms % of lithium. This corresponds to the formula Ag_3Li_{10} and is a most important exception to Hume-Rothery's rules, as no combination of univalent silver and lithium can yield the electron ratio

[56] *Arkiv Kemi, Min., Geol.*, 1933, **11**, [*A*], No. 5, 1; *A.*, 669.

[57] *Ibid.*, No. 10.

[58] *Ann. Physik*, 1933, [v], **16**, 174; *A.*, 341.

[59] *Z. Physik*, 1933, **83**, 291; *A.*, 768.

[60] *Ann. Physik*, 1933, [v], **18**, 150; *A.*, 1110.

[61] W. L. Fink, K. R. van Horn, and P. M. Budge, *Amer. Inst. Min. Met. Eng.* (Inst. Met. Div.), 1931, **93**, 421; *A.*, 1931, 676.

[62] *Z. Krist.*, 1933, **86**, 155; *A.*, 1007.

21 : 13. However, as this is the only example of an alkali γ-structure yet known, it is perhaps unfair to expect the same rules to hold.

In the system manganese–zinc, studied by N. Parravano and V. Caglioti,[63] a γ-structure is also found, corresponding to the formula $Mn_{1\cdot1-2\cdot9}Zn_{11\cdot9-10\cdot1}$. This obeys the rule satisfactorily if we assume that manganese yields no electrons as do iron and platinum, or actually absorbs electrons from the zinc.

The Mn,Al and Cu,Al systems studied by A. J. Bradley and P. Jones[64] are very complicated; so is the FeSn system studied by W. F. Ehret and A. Westgren.[65] FeSn at high temperatures appears to have the NiAs structure. O. Carlsson and G. Hägg[66] have confirmed the extremely complex superstructures found by the author[67] in the CuSn system—the cell of the η-phase contains 500 atoms. S. Stenbeck finds,[68] in a study of the AgHg and AuHg systems, that the γ-structure appears for a formula Ag_5Hg_8, exactly obeying Hume-Rothery's rules. A. Ölander[69] has analysed the very interesting structure of AuCd with a tetragonal deformed cæsium chloride structure which changes above 267° to a true cæsium chloride structure.

A- and B-Group Metals and Their Compounds.—Until recently our knowledge of these was practically confined to the structures of some of the elements. In the last two years this field has, however, attracted much attention, and we are at last in a position to form a fairly general picture of its metal chemistry.

This differs characteristically from that of transition metals and electron compounds. Core interaction is much weaker, leading to large interatomic distances, so that atomic size is an important determinant of crystal type. On the other hand, where B-group elements, particularly of the fifth and sixth group, are concerned, homopolar bonds are common, while compounds between A- and B-group elements sometimes appear to be quasi-ionic : *e.g.*, $Na_4^{+}Pb^{4-}$ or $Mg_2^{2+}Se^{4-}$.

Of the elements themselves, the most interesting new work is on the allotropy of beryllium,[70] calcium,[71] and probably of barium.[72] Yttrium [73] proves to have a hexagonal structure exactly intermediate between strontium and zirconium; consequently it is not clear whether it should be classed as an A-group or a transitional metal. Enough rare-earth metals have been analysed to make the systematic position of the group clear. The structures are all hexagonal, but sometimes also cubic close packed: La (37·0), Ce (34·1), Pr (36·3),[74] Nd (36·1),[75] and Er (36·9) have all the large atomic volume characteristic of the A-group Na (39), or the heavy B-group metals Pb (30), and much larger than those of the transition metals ranging from Zr (23) to Ni (10·9). (The figures in parentheses give atomic volume in $Å.^3$.) Most interesting from the structural point of view is gallium, which has been very carefully redetermined by F. Laves.[76] The structure is not, as believed by earlier workers, tetragonal, but orthorhombic. Each atom is surrounded by seven others: one at 2·45, and two each at 2·70, 2·75, and 2·79 Å. Thus there exist in the solid actual Ga_2 molecules, the first examples discovered in metallic crystals. These molecules persist in the liquid, as has been shown by *X*-ray diffraction,[77] the pattern of which differs completely from that of monatomic liquid mercury. The molecular nature is particularly interesting, as it explains the low melting point, 37°. Hume-Rothery's rule (*Ann. Reports*, 1931, **28**, 294) by which every B-group metal atom should have $8 - N$ neighbours, where N is its group number, seems definitely broken. But only apparently so, for an ideal tetragonal structure can be made up in which each atom has five neighbours, and this by a slight compression distorts into the actual structure with seven neighbours, just as in the case of grey tin of co-ordination number 4 passing into white tin with 6. The close-packed structures of indium and lead show that for larger atoms the generalised metallic attraction is predominant. The transformations of arsenic and antimony from the amorphous into the glassy state have been followed by *X*-rays and electron diffraction.[78]

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[63] *Mem. R. Accad. d'Italia,* 1932, **3,** [Chim.], 5; *A.*, 1932, 1196; *Atti R. Accad. Lincei,* 1931, [vi], **14,** 166; *A.*, 1932, 116.

[64] A. J. Bradley and P. Jones, *Phil. Mag.*, 1931, [vii], **12,** 1137; *A.*, 1932, 116.

[65] *J. Amer. Chem. Soc.*, 1933, **55,** 1339; *A.*, 562.

[66] *Z. Krist.*, 1932, **83,** 308; *A.*, 1932, 1081.

[67] J. D. Bernal, *Nature,* 1928, **122,** 54; *A.*, 1928, 822.

[68] *Z. anorg. Chem.*, 1933, **214,** 16; *A.*, 1006.

[69] *Z. Krist.*, 1932, **83,** 145; *A.*, 1932, 986.

[70] F. M. Jaeger and J. E. Zanstra, *Proc. K. Akad. Wetensch. Amsterdam,* 1933, **36,** 636; *A.*, 1119.

[71] F. Ebert, H. Hartmann, and H. Peisker, *Z. anorg. Chem.*, 1933, **213,** 126; *A.*, 891.

Our knowledge of the compounds of A- and B-group metals we owe mainly to a series of papers by E. Zintl and his collaborators,[79] and also to C. W. Stillwell,[80] A. Baroni,[81] and A. Rossi.[82] The numerous structures studied fall into four main types :

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[72] E. Rinck, *Compt. rend.*, 1931, **193**, 1328; *A.*, 1932, 115.

[73] L. L. Quill, *Z. anorg. Chem.*, 1932, **208**, 59; A., 1932, 1078.

[74] A. Rossi, *Atti R. Accad. Lincei*, 1932, [vi], **15**, 298; *A.*, 1932, 681.

[75] L. L. Quill, *Z. anorg. Chem.*, 1932, **208**, 273; *A.*, 1932, 1192.

[76] *Naturwiss.*, 1932, **20**, 472; *A.*, 1932, 797; *Z. Krist.*, 1933, **84**, 256.

[77] F. Sauerwald and W. Teske, *Z. anorg. Chem.*, 1933, **210**, 247; *A.*, 341.

[78] E. G. Bowen and W. M. Jones, *Phil. Mag.*, 1932, [vii], **13**, 1029; *A.*, 1932, 567; C. W. Stillwell and L. F. Audrieth, *J. Amer. Chem. Soc.*, 1932, **54**, 472; *A.*, 1932, 479; G. R. Levi and D. Ghiron, *Atti R. Accad. Lincei*, 1933, [vi], **17**, 565; *A.*, 1003; J. A. Prins, *Nature*, 1933, **131**, 760; *A.*, 657; A. Schulze and L. Graf, *Metallwirt.*, 1933, **12**, 19; *A.*, 1109.

(1) The simplest is the CsCl type, which appears for LiAg, LiTl, LiHg, MgAg, MgTl, CaTl, and SrTl.

(2) NaTl structure. This is a very interesting new structure. The cell is a double body-centred structure with 8 atoms of each kind. But each kind of atom occupies the positions of a diamond lattice (000, $\frac{1}{4}\frac{1}{4}\frac{1}{4}$, etc. and $\frac{1}{2}\frac{1}{2}\frac{1}{2}$, $\frac{3}{4}\frac{3}{4}\frac{3}{4}$, etc.). Each atom has therefore four neighbours of its own kind and four of the other kind, all at the same distance. It is clear that such a structure should only occur when the atomic radii of both atoms are nearly alike. It is, in fact, found for LiZn, LiCd, LiGa, LiIn, NaIn, and NaTl, where the greatest radius difference is 0·2 Å. Thus in these compounds the alkali metals appear to be compressed down to the size fixed by this B-group metal.

(3) A number of alloys of formula AB_3, where A is Ca, Sr, La, and Ce, and B is Sn, Tl, or Pb, form cubic structures based on a face-centred lattice of B in which one atom is replaced by A.

(4) Mg_2Ge, Mg_2Sn, and Mg_2Pb have the anti-CaF_2 structure. Other more complex structures have been found, as KBi_2 with the $MgCu_2$ structure, a framework of bismuth atoms in the large holes of which are the potassium atoms; and Na_4Pb, $LaAl_4$, and Li_4Sn with large cells.

Sub-metallic.

Adamantine Compounds.—The structure of the hexaborides of formula B_6M, where M = Ca, Sr, Ce, etc., mentioned in the last report as possessing an anomalous ion B_8^{2-}, has now been shown by F. Laves[83] to be really adamantine, consisting of a covalent-linked B lattice with the metal atoms in the interstices. Each B atom has five B neighbours, one at 1·66 and four at 1·76 Å., and four metal neighbours. Each metal atom has 24 B neighbours. This 4 : 24 co-ordination is the highest yet found. Essentially similar compounds have been shown by A. Schleede and M. Wellmann[84] to be formed by the action of alkali metals on graphite. Compounds C_8K and $C_{16}K$ are formed with potassium atoms between each layer or between alternate layers of the normal graphite structure. All kinds of carbon so far examined have been shown to possess a graphite structure. The differences between the physical and chemical properties of different varieties are mainly due to the crystal size, which may in the extreme case of highly active carbon from benzene be only three layers thick and six condensed benzene rings wide, as U. Hofmann[85] has shown. Other work[86] shows the importance of the edges of the crystallites in absorption and catalytic activity.

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[79] *Z. physikal. Chem.*, 1932, [*B*], **16**, 183, 195, 206; *A.*, 1932, 455; *ibid.*, 1933, [*B*], **20**, 245, 272; *A.*, 562; *Z. anorg. Chem.*, 1933, **211**, 113; *A.*, 472; *Z. Elektrochem.*, 1933, **39**, 81, 84, 86; *A.*, 341.

[80] C. W. Stillwell and W. K. Robinson, *J. Amer. Chem. Soc.*, 1933, **55**, 127; *A.*, 218.

[81] *Atti R. Accad. Lincei*, 1932, [vi], **16**, 153; *A.*, 18.

[82] *Ibid.*, 1933, [vi], **17**, 182, 839; *A.*, 558, 1003.

[83] *Z. physikal. Chem.*, 1933, [B], **22**, 114; *A.*, 891.

Homopolar Crystals of Fifth- and Sixth-group Elements.—Through the work of the last two years the gap represented by our ignorance of the structures of this important group of " sulphide ores " has been largely abolished. It is now possible to present a fairly ordered picture of structure types, and to begin to construct a thio-chemistry equivalent to the oxygen chemistry of the silicates. Thio-structures differ from oxy-structures, owing to the larger size and greater polarisability of the S (Se, P, As, etc.) atoms, so that except for alkali compounds they are not ionic. The packing is generally closer, owing to increased van der Waals forces, but this is offset by the smaller co-ordination number of the metal atoms—generally 4 or 6. The homopolar bonds formed are easily ionised, giving the whole crystal a metallic or semi-metallic character. Sulphide ores have long been studied by means of their reflecting power, and recently F. C. Phillips[87] has shown that, just as in the case of ionic crystals, the molecular refractivities calculated from the reflecting power are additive functions of those of the atoms. This shows the relative unimportance of structural considerations. On the whole, the structures correspond to those of simple oxides or halides. Thio-salt complex groups, such as SbS_4, do not exist in the crystal as separate individuals, but fuse into chains or networks. The general scheme can be set out as follows in order of increasing sulphur content. References are only given to structures determined in the last two years.

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[84] *Z. physikal. Chem.*, 1932, [*B*], **18**, 1; *A.*, 1932, 903.

[85] U. Hofmann and D. Wilm, *ibid.*, p. 401; *A.*, 1932, 1078; U. Hofmann and A. Frenzel, *Kolloid-Z.*, 1932, **58**, 7; *A.*, 1932, 217; U. Hofmann and W. Lemcke, *Z. anorg. Chem.*, 1932, **208**, 194; *A.*, 1932, 1212; S. B. Hendricks, *Z. Krist.*, 1932, **83**, 503; *A.*, 12.

[86] E. Berl, K. Andress, L. Reinhardt, and W. Herbert, *Z. physikal. Chem.*, 1932, **158**, 273; *A.*, 1932, 217; E. Berl and R. Bemmann, *ibid.*, **162**, 71; *A.*, 142; H. Arnfelt, *Arkiv Mat., Astron. Fysik*, 1932, **23**, [*B*], No. 2, 1; *A.*, 1932, 903; P. M. Wolf and N. Riehl, *Angew. Chem.*, 1932, **45**, 400; *A.*, 1932, 803; E. N. Greer and B. Topley, *Nature*, 1932, **129**, 904; *A.*, 1932, 795.

[87] *Min. Mag.*, 1933, **23**, 458.

A_2B. Ag_2S, Cu_2S.

A_3B_2, (1). Zn_3P_2[88] type also for Zn_3As_2, Cd_3P_2, Cd_3As_2; cubic, $a =$ 12 Å., 16 mol. per cell.

(2). Mg_3Sb_2 type,[89] also for Mg_3Bi_2; hexagonal anti-A sesquioxide (La_2O_3) structure (for the ionic Mg_3P_2 structure, see p. 400).

A_4B_3. Co_4S_3,[90] and Cu_3FeS_3 (bornite); cubic, $a = 10$ Å.

AB, (1). Rock-salt type, 6-co-ordinated (Mg, Ca, Sr, Ba, Pb, Mn) (S, Se, Te); all the sulphides except those of Pb and Mn are ionic.

(2). Types related to (1); HgS (cinnabar), GeS (SnS),[91] $Ag(SbBi)S_2$ (aramaoite).

(3). Blende and wurtzite types, 4-co-ordinated (Be, Zn, Cd, Hg, Mn) (S, Se, Te), (Al, Ga) (N, P, As, Sb). It is interesting to note that MnS[92] exists in the three forms, rock-salt, blende, and wurtzite, showing that they do not differ fundamentally in nature.

(4). Types related to blende; $CuFeS_2$[93] (chalcopyrite), $KFeS_2$;[94] Cu_3VS_4 (sulvanite). This structure, as determined by L. Pauling,[95] is very anomalous, for the four metal atoms surrounding the sulphur are all on one side of it.

(5). Nickel arsenide type, (Mn, Fe, Co, Ni) (S, Se, Te, As, Sb). This is the typical form for monosulphides, etc., of the iron group, and is essentially metallic in character.

(6). Intermediate structures. The sulphides of Ni, Cu, Pd, Pt form structures of some complexity and unusual co-ordination. NiS (millerite) has a 5 : 5-co-ordination. CuS (covelline) is a bright blue mineral strongly pleochroic; the structure, determined by I. Oftedal,[96] helps to explain these properties. It is really a compound of Cu_2S and CuS_2 arranged in layers containing free sulphur atoms as well as S_2 molecules.

The structure of PtS (cooperite), determined by F. A.

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[88] M. von Stackelberg and R. Paulus, *Z. physikal. Chem.*, 1933, [*B*], **22,** 305; *A.*, 1003.

[89] E. Zintl and E. Husemann, *ibid.*, [*B*], **21,** 138; *A.*, 558.

[90] V. Caglioti and G. Roberti, *Gazzetta*, 1932, **62,** 19; *A.*, 1932, 326.

[91] W. H. Zachariasen, *Physical Rev.*, 1932, [ii], **40,** 917; *A.*, 1932, 903.

[92] H. Schnaase, *Naturwiss.*, 1932, **20,** 640; *A.*, 1932, 986; *Z. physikal. Chem.*, 1933, [*B*], **20,** 89; *A.*, 341.

[93] L. Pauling and L. O. Brockway, *Z. Krist.*, 1932, **82,** 188; *A.*, 1932, 682.

[94] H. O'Daniel, *ibid.*, 1933, **86,** 192; *A.*, 1106.

[95] L. Pauling and R. Hultgren, *ibid.*, 1933, **84,** 204; *A.*, 215.

[96] *Ibid.*, 1932, **83,** 9; *A.*, 1932, 987.

Bannister,[97] is interesting as showing platinum surrounded by four sulphur atoms in a plane instead of a tetrahedron. (Pd, Pt, Ni)S with a more complicated structure has been called *braggite*, being the first mineral discovered by *X*-ray analysis.

A_3B_4, Spinel type. There may be as many sulphides as oxides of this type, which is that of Co_3S_4 and Ni_3S_4. Fe_3S_4 does not, however, appear to be stable,[98] though $(FeNi)_3S_4$ (daubreelite) is found in meteorites.[99] More complex spinels studied by L. Passerini [1] are $MnCr_2S_4$, $CdCr_2S_4$, and $ZnCr_2S_4$.

A_2B_3, Stibnite type. The extremely important structure of Sb_2S_3 and Bi_2S_3 has at last been analysed, by W. Hofmann.[2] The crystals are orthorhombic; *a*, *b*, *c* are 11·20, 11·28, 3·83 Å., containing four molecules, space group D_{2h}^{16}–*Pbnm*, with all the atoms on the symmetry planes. The most important feature is the existence of bands of antimony and sulphur atoms linked by primary valencies lying along the *c*-axis in the (010) plane. This explains at the same time both the needle-shaped habit and the excellent cleavage, and is most interesting among the sulphides as analogous to the asbestos-like structures in the silicates.

ABC_2. The structure of Sb_2S_3 is repeated in some thioantimonates also studied by Hofmann;[3] $CuSbS_2$ and $CuBiS_2$ contain Sb–S chains: that of $AgSbS_2$ and $TlAsS_2$ is more complicated.

Other thioantimonates. Bournonite, $CuPbSbS_3$,[4] and stephanite, Ag_5SbS_4,[5] have also been studied, but no complete structure has been arrived at.

AB_2, (1). Pyrite and marcasite type (Mn, Fe, Co, Ni, Ru, Rh, Pd, Os, Ir, Pt) (S_2, SAs, As_2). Here the non-metal atoms are arranged in molecules. H. Parker and W. Whitehouse [6] have made a very exact Fourier analysis of FeS_2; Fe is found to carry 26 electrons, indicating the essentially non-ionic nature of this compound. The distance S–S is 2·14 Å., and Fe–S is 2·26 Å. Similar conclusions were reached by M. Buerger [7] for $FeAs_2$, which has the marcasite structure.

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[97] *Min. Mag.*, 1932, **23**, 188; *A.*, 1932, 1014.

[98] See refs. 23 and 24 (p. 385).

[99] F. Heide, E. Herschkowitz, and E. Preuss, *Chem. Erde*, 1932, **7**, 483; *A.*, 1932, 1230.

[1] L. Passerini and M. Baccaredda, *Atti R. Accad. Lincei*, 1931, [vi], **14**, 33; *A.*, 1932, 114; G. Natta and L. Passerini, *ibid.*, p. 38; *A.*, 1932, 114.

[2] *Z. Krist.*, 1933, **86**, 225; *A.*, 1106; J. G. Albright, *Physical Rev.*, 1931, [ii], **37**, 458; *A.*, 215.

[3] *Fortschr. Min., Krist. Petr.*, 1932, **17**, 422; *A.*, 1029; *Z. Krist.*, 1933, **84**, 177; *A.*, 214.

[4] I. Oftedal, *ibid.*, 1932, **83**, 157; *A*, 1932, 987.

[5] R. Salvia, *Anal. Fis. Quim.*, 1932, **30**, 416; *A.*, 1932, 904.

(2). Cadmium iodide type (Ti, Zr, Sn, Pt) (S_2, Se_2, Te_2).

(3). Molybdenum sulphide type, MoS_2, WS_2. Both of these are layer lattices.

It is clear that this survey of the sulphides is not complete, but it does at any rate show the main lines on which sulphur compounds are built.

Ionic Crystals.

The interest in ionic crystals continues unabated—over 250 papers have been published on them alone—but as now the main structural types have been fixed, interest has shifted to points with other than purely crystallographic interest, such as the relations of oxides and hydroxides, the rôle of water, or the structure of complex ions.

Halides, Oxides, and Hydroxides.—A new fact has been added to the structural relations of the alkali halides by G. Wagner and L. Lippert's [8] observation that cæsium chloride changes its structure into that of sodium chloride above 450°. The small energy difference between these structures is thus experimentally confirmed.

The most interesting halide structures which have been investigated recently are those of cadmium, mercury, and lead. J. M. Bijvoet and W. Nieuwenkamp [9] have shown that cadmium bromide, which, when sublimed has the cadmium chloride structure, when precipitated appears in the form of a statistical mixture of the chloride and the iodide structure; the interleavings cannot be more than of the order of one or two layers thick. Incidentally, O. Hassel [10] has shown that the actual structure of cadmium iodide has a cell double that of the hitherto accepted structure. Complete analyses have also been made of the structures PbF_2,[11] $PbCl_2$,[12]

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[6] *Phil. Mag.*, 1932, [vii], **14**, 939; *A.*, 13.

[7] *Z. Krist.*, 1932, **82**, 165; *A.*, 1932, 682.

[8] *Z. physikal. Chem.*, 1933, [*B*], **21**, 471; *A.*, 768.

[9] *Chem. Weekblad*, 1933, **30**, 479; *A.*, 892; *Z. Krist.*, 1933, **86**, 466.

[10] *Z. physikal. Chem.*, 1933, [*B*], **22**, 333; *A.*, 1004.

[11] J. A. A. Ketelaar, *Z. Krist.*, 1932, **84**, 62; *A.*, 215.

[12] H. Braekken, *ibid.*, **83**, 222; *A.*, 1932, 1079.

$PbBr_2$,[13] PbClF,[14] PbBrF.[15] The first three are isomorphous. They may be considered as layer lattices which have been distorted into an approximation to a fluoride 8 : 4-co-ordination structure, owing to the large size and polarisability of the cation. Actually, the co-ordination is 9 : 4 or 5, each lead atom having three bromine atoms at 3·0 and three at 3·2 Å., all on one side, while on the other it has one at 3·3 and two at 4·1 Å. There is no evidence for a semi-molecular association of lead bromide. The chlorofluoride structure is particularly interesting as a typical sandwich structure, layers of lead fluoride in fluorite arrangement alternating with a lead chloride layer lattice of the tetragonal lead oxide type. Curiously enough, lead chlorofluoride has been known for a long time as the mineral matlockite Pb_2OCl_2, but its *X*-ray pattern led to its identification, and a new analysis showed that fluorine had been taken for oxygen. H. Braekken[16] has shown that mercuric bromide has a somewhat complicated layer structure also without molecules.

More work has been done on AX_3 compounds. The trifluorides of Al, Fe, Co, Rh, Pd, etc., do not, like the trichlorides, form close-packed layer lattices,[17] but approximate to a cubic lattice whose corners are occupied by the cations, while the anions occupy the mid-point of an edge between two cations. The structure of aluminium fluoride, analysed by J. A. A. Ketelaar,[18] shows a rhombohedral cell containing two such units distorted in an attempt to fill the large holes in the cell centres. These holes can be occupied with water in the zeolite fashion; $2AlF_3,H_2O$ only loses its molecule of water at a red heat.

N. Wooster[19] has pointed out the essential isomorphism between ferric fluoride and tungsten trioxide (see *Ann. Reports*, 1931, **28**, 296), with which rhenium trioxide[20] has been shown to be isomorphous. These two structures are the analogues in 6 : 2-co-ordination of the 4 : 2-co-ordination structures of beryllium fluoride and silica. As in them, the cation can be replaced by one of lower charge, the extra charge being made up by an ion in the vacant spaces. Thus

$Si_2^{4+}O_4$	$K^+Al^{3+}Si^{4+}O_4$	Nephelene
$Al^{3+}F_3$	$Na^+Mg^{2+}F_3$	Perovskite structure
$W^{6+}O_3$	$Na^+Ta^{5+}O_3$	

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[13] W. Nieuwenkamp and J. M. Bijvoet, *Z. Krist.*, 1932, **84**, 49; *A.*, 215.

[14] *Idem*, *ibid.*, **81**, 469; *A.*, 1932, 450; *ibid.*, 1933, **86**, 470.

[15] *Ibid.*, 1932, **82**, 157; *A.*, 1932, 681.

[16] *Ibid.*, 1932, **81**, 152; *A.*, 1932, 218.

[17] N. Wooster, *ibid.*, 1932, **83**, 35; *A.*, 1932, 986.

[18] *Ibid.*, 1933, **85**, 119; *A.*, 450.

[19] *Ibid.*, **84**, 320; *A.*, 214.

[20] K. Meisel, *Z. anorg. Chem.*, 1932, **207**, 121; *A.*, 1932, 903.

A stranger case is that of the tungsten bronzes studied by W. F. de Jong :[21] here the neutral WO_3 structure takes up a variable amount of metallic sodium in its interstices, giving highly coloured compounds whose physical properties would be worth investigating. Another form of substitution is the replacement of two cations by one of higher and one of lower charge. Thus, as Goldschmidt predicted, BPO_4 and $BAsO_4$[22] have essentially the cristobalite structure of silica. This is particularly interesting, as in most compounds boron appears as 3-co-ordinated.

The cristobalite structure, the cubic high-temperature form of silica, has been much studied. T. F. W. Barth[23] has shown that both in cubic β-, stable above 240°, and orthorhombic α-cristobalite, the oxygen atoms do not lie, as was previously thought, on the line between two silicons, but definitely to one side. Thus, in all cases where oxygen is found co-ordinated to two cations, we find that the lines joining it to them are always inclined at about 140°, indicating the effect of covalent binding tending towards a valency angle of 109°. I. Levin and E. Ott[24] first noticed that opal contains at ordinary temperatures β- or high-temperature cristobalite. As R. B. Sosman[25] has shown, here can be no question of delayed inversion. J. Grieg,[26] however, has pointed to the probable explanation. In opal, as in some glasses, the cristobalite is closely adherent to an amorphous matrix. Now, at transition from β- to α-, there is normally a contraction of about 4% by volume. Either, therefore, the β-cristobalite inverts and breaks away from its matrix, as it has been observed to do in certain circumstances, or it fails to invert and continues to exist as the stable form under permanent tension (negative pressure) from the matrix. In the Reporters' opinion this negative pressure is sufficient to account for the appearance of β-cristobalite rather than any other form of silica—all with smaller specific volumes—in the slow dehydration of massive silica gel, even if the temperature has never been above the $\beta \rightarrow \alpha$ transformation point at 198—270°. If this is so, it offers some interesting possibilities for finding the negative-pressure forms of other materials. Through the work of M. von Stackelberg and R. Paulus[88 (cf. 89)] we know some of the properties of the ions N^{3-}, P^{3-}. The compounds Mg_3N_2, Ca_3N_2, Mg_3P_2, etc., are ionic in character and have been shown to possess the anti-C-sesquioxide type: *i.e.*, the ions Mg^{2+} and N^{3-} occupy respectively the positions of O^{2-} and Mn^{3+} in Mn_2O_3. From this, the radii of N^{3-} and P^{3-} are found to be 1·4 and 1·85 Å., very slightly larger than those of O^{2-} and S^{2-} respectively. The free ions have, of course, far larger radii, but their extreme compressibility almost compensates for this.

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[21] *Z. Krist.*, 1932, **81**, 314; *A.*, 1932, 450; *ibid.*, 1932, **83**, 496; *A.*, 12.

[22] G. E. R. Schulze, *Naturwiss.*, 1933, **21**, 562; *A.*, 1004.

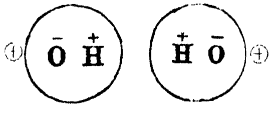
[23] *Amer. J. Sci.*, 1932, [v], **23**, 350; **24**, 97; *A.*, 1932, 564, 903.

[24] *Z. Krist.*, 1933, **85**, 305; *A.*, 666; cf. F. P. Dwyer and D. P. Mellor, *J. Proc. Roy. Soc. New South Wales*, 1933, **66**, 378; *A.*, 691.

[25] *J. Amer. Chem. Soc.*, 1932, **54**, 3015; *A.*, 1932, 903.

[26] *Ibid.*, p. 2846; *A.*, 1932, 903.

We are now beginning to see the place of hydroxides in crystal chemistry. The strongly polar nature of the hydroxyl group (OH) leads in every case so far examined to a position unsymmetrically surrounded by cations, and in particular to layer lattices. The structure of lithium hydroxide determined by T. Ernst [27] proves to be the simplest tetragonal layer lattice of the lead oxide type. Aluminium hydroxide (hydrargillite) is also a layer lattice, but the structure determined by (Miss) H. D. Megaw [28] is far more complex. Zinc hydroxide in its stable form, analysed by R. Corey and R. W. G. Wyckoff,[29] is not a layer lattice, but each hydroxyl is surrounded by two zinc atoms on one side and two hydroxyl ions on the other, while each zinc has four hydroxyl neighbours. An unstable form exists with a layer lattice, as shown by W. Feitknecht,[30] and this forms sandwich structures with zinc halides, carbonates, and sulphates.



In all cases there seems to be a definite attraction between two hydroxyl groups attached ot different cations, as shown in the inset, and this attraction increases with the polarising power of the cation, and consequently with the degree of polarisation of the hydroxyl group, as shown by the decrease in inter-hydroxyl distances (Å.) in the series

$$Li(OH)\ (3{\cdot}61) \quad Ca(OH)_2\ (3{\cdot}36) \quad Mg(OH)_2\ (3{\cdot}22)$$
$$Zn(OH)_2\ (2{\cdot}83) \quad Al(OH)_3\ (2{\cdot}79) \quad B(OH)_3\ (2{\cdot}65)$$

It is clear that the apparent neutrality of the hydroxyl groups to each other in lithium hydroxide has been replaced by a powerful attraction in the case of boric acid, which is only less than that of hydrogen-bond-linked oxygens of acids, 2·55 Å. (see *Ann. Reports*, 1931, **28**, 291). This new kind of bond, which may be called the double hydrogen bond, still requires theoretical explanation, as the simple dipole effect should give increased repulsion rather than attraction.

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[27] *Naturwiss.*, 1932, **20**, 124; *A.*, 1932, 326; *Z. physikal. Chem.*, 1933, [*B*], **20**, 65; *A.*, 341.

[28] *Z. Krist.*, in press.

[29] *Ibid.*, 1933, **86**, 8; *A.*, 1003.

[30] *Ibid.*, 1932, **84**, 173; *A.*, 214; *Helv. Chim. Acta*, 1933, **16**, 427; *A.*, 664.

A most fascinating field has been opened in the study of the conversion of hydroxides into oxides. The mechanism in magnesium hydroxide has been already commented on (see p. 386). That of the trihydroxides of aluminium and iron is yet more complicated and interesting. This has been investigated by a great number of workers, by *X*-ray and magnetic methods. Both metals form two series of hydroxides and oxides, usually known as α and γ. In each series are a trihydroxide $M(OH)_3$, a monohydroxide $MO(OH)$, and an oxide M_2O_3. Relationships between them are shown in the scheme :

	α.	γ.
$Al(OH)_3$	Structures unknown	Hydrargillite (17·6)
$Fe(OH)_3$		γ-$Fe(OH)_3$, structure unknown
$AlO(OH)$	Diaspore (14·7)	Böhmite
$FeO(OH)$	Goethite (17·25)	Lepidocrocite (18·2) [$Fe(OH)_2$]
Al_2O_3	Corundum (14·2)	γ-Al_2O_3 (13·9)
Fe_2O_3	Hæmatite (16·9)	Ferromagnetic Fe_2O_3 (17·1) [Fe_3O_4]

The figures in parentheses are the volumes occupied per oxygen atom. The value for close-packed oxygen atoms would be 13·7 Å.^{3}.

The α-series is the more stable with smaller atomic volume; the γ-series, on the other hand, is the one usually formed from precipitation, and is more chemically active. The structure of the α-trihydroxides has not been determined; it may be similar to that of zinc hydroxide. That of the α-monohydroxides, diaspore and goethite, has been established by M. Deflandre[34 (p. 386), 31] and S. Goldsztaub.[32] It is essentially a structure of hexagonal close-packed oxygens with metal atoms in octahedral holes. Oxygens and hydroxyls are distinguished by being symmetrically or asymmetrically surrounded by metal atoms. On dehydration, it passes into a parallel aggregate of corundum or hæmatite crystals, a structure similarly close packed.

The γ-trihydroxides, hydrargillite and γ-$Fe(OH)_2$, are layer structures (see above, p. 401); on dehydration, they pass without loss of crystal structure into the monohydroxides böhmite (the chief mineral of bauxite ores) and lepidocrocite (rubinglimmer or common rust).[33] The structure of these is not fully worked out, but it is clearly a layer lattice cleaving readily, probably across double hydrogen bonds. Its birefringence is strongly negative, 0·57, while

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[31] Cf. K. Takane, *Proc. Imp. Acad. Tokyo*, 1933, **9**, 113; *A.*, 558.

[32] *Compt. rend.*, 1932, **195**, 964; *A.*, 13; W. H. Albrecht and E. Wedekind, *Z. anorg. Chem.*, 1931, **202**, 205; *A.*, 1932, 134.

[33] S. Goldsztaub, *Compt. rend.*, 1931, **193**, 533; *A.*, 1931, 1390.

[34] G. Schikorr, *Z. anorg. Chem.*, 1933, **212**, 33; *A.*, 581; R. D. Williams and J. Thewlis, *Trans. Faraday Soc.*, 1931, **27**, 767; *A.*, 1932, **32**; A. Girard and G. Chaudron, *Compt. rend.*, 1933, **196**, 925; *A.*, 581.

that of goethite is only 0·14 [35 (p. 386)]. Lepidocrocite is also formed by the oxidation of $Fe(OH)_2$,[34] by the normal rusting of iron,[35] and by the hydrolysis of ferrites [36] (MO,Fe_2O_3) into which it, but not goethite,[37] can be reversibly reconverted. On dehydration, böhmite and lepidocrocite pass into a parallel aggregate of γ-Al_2O_3 or γ-Fe_2O_3, cubic with a spinel structure [38] containing extra oxygen atoms (see *Ann. Reports*, 1931, **28**, 299). The γ-Fe_2O_3 structure holds these oxygen atoms so loosely that it loses them in a vacuum even at 250° and is turned into magnetite, Fe_3O_4.[36] In oxygen, on the other hand, it changes at about 600° into the stable α-Fe_2O_3 form. Lepidocrocite is also, as might be expected from its larger volume, unstable to pressure. O. Baudisch [39] has shown that it may be converted into α-Fe_2O_3 by grinding at room temperature. $Fe(OH)_2$ is also unstable, undergoing slow autoxidation even when kept under anaërobic conditions.

The most striking property distinguishing the α- and the γ-series is ferromagnetism, which is characteristic of the latter. The occurrence of this phenomenon in purely ionic compounds is of great theoretical interest, particularly from the point of view of their magneto-optics, but so far no single-crystal work has been reported. Apart from the γ-series, a number of ferrites show ferromagnetic properties. The nature of these ferrites has been studied, especially by H. Forestier [42] and S. Hilpert.[40] They are all of the mixed oxide type, of general formula $m\text{MO},n\text{Fe}_2\text{O}_3$, where M is Li_2, Na_2, K_2, Be, Mg, Cu, Sr, Ba, Mn, Fe, Co, Ni, Cu, Zn, Pb, $Al_{2/3}$, $Sn_{1/2}$. Most of these are ferromagnetic, some with exceptionally low Curie points: for $LiFeO_2$ and $NaFeO_2$ it lies below − 70°. Some have special structures, *e.g.*, $LiFeO_2$ with a rock-salt structure with iron and lithium indistinguishable (see p. 382), $NaFeO_2$ [41] with a layer lattice of FeO_2' separated by large $Na^\cdot$ ions, and α-$BeFe_2O_4$ [42] with a lepidocrocite structure with beryllium replacing two hydrogens. The great majority have spinel-like structures, but with extremely variable composition, $SrO,2Fe_2O_3$ showing the same structure as $SrO,9Fe_2O_3$, suggesting that the structure is simply a stabilised γ-Fe_2O_3 structure. It is interesting to note that the maximum of ferromagnetism is not reached for the true spinel MO,Fe_2O_3, but for an iron-richer solid solution $2MO,3Fe_2O_3$. Others, such as $2MnO,3Fe_2O_3$, β-BeO,Fe_2O_3, and SnO_2,Fe_2O_3, show the α-Fe_2O_3 structure, and are not ferromagnetic. It seemed natural to conclude that the ferromagnetism was a structural property of the γ-series, but there are several indications that this is not the case,[39, 40] notably the work of G. Kurdjumov and his collaborators,[43] who prepared ferromagnetic α-Fe_2O_3 in an alloy. It is more probable that here, as in metallic ferromagnetics, structure plays a secondary rôle, the internal electronic state of the ion being primary. In ionic compounds ferromagnetism seems to be associated with the state of iron functioning as ferrous acid, probably the net acid γ-$FeO_2{}'\,H^{\bullet}$. It is noticeable that the oxidation product of $Fe(OH)_2$ is ferromagnetic or not, according as the medium is alkaline or acid.[34]

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[35] J. Cates, *Trans. Faraday Soc.*, 1933, **29**, 817; *A.*, 1022.

[36] A. Girard and G. Chaudron, *Compt. rend.*, 1931, **193**, 1418; *A.*, 1932, 133.

[37] A. Krause, Z. Czapska, and J. Stock, *Z. anorg. Chem.*, 1932, **204**, 385; *A.*, 1932, 481.

[38] H. B. Barlett, *J. Amer. Ceram. Soc.*, 1932, **15**, 361; *A.*, 1932, 904; R. Brill, *Z. Elektrochem.*, 1932, **38**, 669; *A.*, 1932, 1004.

[39] O. Baudisch and L. A. Welo, *Naturwiss.*, 1933, **21**, 593, 659; *A.*, 1022, 1131.

[40] S. Hilpert and A. Wille, *Z. physikal. Chem.*, 1932, [*B*], **18**, 291; *A.*, 1932, 985; S. Hilpert and A. Lindner, *ibid.*, 1933, [*B*], **22**, 395; *A.*, 1234.

[41] S. Goldsztaub, *Compt. rend.*, 1933, **196**, 280; *A.*, 215.

[42] H. Forestier and M. Galand, *ibid.*, 1931, **193**, 733; *A.*, 1932, 30.

The oxide–hydroxide relations of cobalt [44] are essentially similar to those of iron; those of manganese are more complicated, as solid transformations between Mn^{2+}, Mn^{3+}, and Mn^{4+} are all possible. The transformations

$Mn(OH)_2 \longrightarrow$	$MnO(OH) \longrightarrow$	MnO_2
Pyrochroite	Manganite	Pyrolusite (Polianite)
$Mg(OH)_2$	α-$AlO(OH)$	TiO_2
Structure	Pseudo-structure	Rutile structure

all take place without any essential change in crystal structure.[45] The products in all these cases are, however, microcrystalline, as they are formed below their recrystallising temperatures: they consequently possess large surface and high chemical reactivity. These oxide–hydroxide transformations are beginning to become intelligible through crystal analysis. It should now be possible to attack the related problem of the colloidal hydroxides (*e.g.*, those of aluminium, iron, manganese, etc.) so important for physical, bio- and geo-chemistry.

Mixed Oxides.—Of mixed oxides the spinel structures have already been discussed (see p. 382). The more complex structures of the pyrochlorite group have also been much studied. This structure bids fair to rival that of spinels in its stability and variety of composition. Its essential formula is $[A]_2^{6-8}[B]_2^{6}O_7$ (see *Ann. Reports*, 1931, **28**, 299), with a cubic cell $a \simeq 10{\cdot}3$ Å., but the structure can take up at least one atom of oxygen and four of water without swelling noticeably. The essential feature of the structure is the 6-co-ordinated Sb^{5+} ion (which may be replaced by Nb^{5+}, Ta^{5+}, Ti^{4+} etc.). As L. Pauling [46] has pointed out, antimony never appears in any less than 6-co-ordination, and among acid-forming ions we should distinguish sharply between the 3-co-ordination of $(B)^{3+}$, C^{4+}, N^{5+}, the 4-co-ordination of $(Al)^{3+}$, Si^{4+}, $(Ge)^{4+}$, P^{5+}, As^{5+}, S^{6+}, Se^{6+}, Cl^{7+}, Br^{7+}, V^{5+}, Cr^{6+}, Mn^{7+} and the 6-co-ordination of Sn^{4+}, Sb^{5+}, Te^{6+}, I^{7+}, Fe^{3+}, Ti^{4+}, $(Zr)^{4+}$, Nb^{5+}, Ta^{5+}, Mo^{6+}, W^{6+}, Re^{7+}. (The elements in parentheses are borderline cases; Mo^{6+} and W^{6+} are anomalous.) G. Natta and M. Baccaredda [47] have shown that not only some but all the calcium atoms in $Ca_2Sb_2O_7$ can be replaced by $\frac{1}{2}Sb_2O$, so that the structure of Sb_2O_4 really belongs to the pyrochlorite group, and should be written as $Sb^{3+}_2Sb^{5+}_2O_8$, just as Fe_3O_4 is $Fe^{2+}Fe^{3+}_2O_4$. Further work on this group has been done by F. Machatschki [48] and others.[49]

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[43] V. Danilov, G. Kurdjumov, E. Pluschnik, and T. Stellezky, *Naturwiss.*, 1933, **21**, 177; *A.*, 340.

[44] H. B. Weiser and W. O. Milligan, *J. Physical Chem.*, 1932, **36**, 722; *A.*, 1932, 485.

[45] G. Vaux, private communication.

Silicates.—Since the main outlines of silicate chemistry are known [50] (*Ann. Reports*, 1931, **28**, 301), most of the work done in the past two years has been concerned with anomalous or very complex silicates, of mineralogical rather than of chemical interest. The exception is the determination by W. H. Taylor [51] of the structure of sanidine, $(K,Na)AlSi_3O_8$, which gives the key to that of the petrologically essential group the felspars, and thus closes the last important gap in our knowledge of silicate types. As anticipated, it proves to be based on a somewhat collapsed $(Si_3AlO_8)^{1-}$ framework, in the interstices of which are found the alkali atoms. Among the more complicated silicates studied are those of hemimorphite [52] and bertrandite [53] by T. Ito and J. West, euclase by J. Biscoe and B. Warren,[54] and zunyite by L. Pauling.[55] All are hydroxy-silicates, but in no case are the hydroxyl ions attached to silicon, but to zinc, beryllium, or aluminium. The silicate grouping is different in each case. Hemimorphite, $Zn_4(OH)_2Si_2O_7,H_2O$, is a hydrous hydroxy-disilicate. Bertrandite, $2BeO,2Be(OH)SiO_3,SiO_4$, contains three tetrahedron chains and independent orthosilicate ions. Euclase, $AlBe(OH)SiO_4$, is an orthosilicate containing tetrahedral $BeO_2(OH)$ and octahedral $AlO_3(OH)$ chains. Each hydroxyl is shared by a beryllium and an aluminium neighbour. Zunyite, $[Al]^6_{12}O_2[(OH)F]_{18}[Al]^4O_2Si_5O_{16}Cl$, contains both 6- and 4-co-ordinated aluminium, as well as a complex $(Si_5O_{16})^{12-}$ group and interstitial chlorine.

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[46] *J. Amer. Chem. Soc.*, 1933, **55**, 1895; *A.*, 664.

[47] *Atti R. Accad. Lincei*, 1932, [vi], **15**, 389; *A.*, 1932, 829; *Z. Krist.*, 1933, **85**, 271.

[48] *Chem. Erde*, 1932, **7**, 56; *A.*, 1932, 596; *Zentr. Min. Geol.*, 1932, 33; *A.*, 1932, 1079; F. Machatschki and O. Zedlitz, *Z. Krist.*, 1932, **82**, 72; *A.*, 1932, 682.

[49] O. Zedlitz, *Z. Krist.*, 1932, **81**, 253; *A.*, 1932, 450; E. Reuning, *Chem. Erde*, 1933, **8**, 186; *A.*, 1029; G. Aminoff with R. Blix, *K. Svenska Vetenskaps Akad. Handl.*, 1933, [iii], **11**, No. 4, 3, 14; *A.*, 482.

[50] E. Schiebold, *Ergeb. exakt. Naturwiss.*, 1932, **11**, 352; *A.*, 369; P. Niggli and E. Brandenberger, *Z. Krist.*, 1932, **82**, 210; *A.*, 1932, 682; F. Machatschki, *Geol. För. Förh.*, 1932, **54**, 447; *A.*, 1137.

[51] *Z. Krist.*, 1933, **85**, 425; *A.*, 892.

[52] *Ibid.*, 1932, **83**, 1; *A.*, 1932, 987.

[53] *Ibid.*, p. 384; *A.*, 13.

[54] *Ibid.*, 1933, **86**, 292; *A.*, 1107.

[55] *Ibid.*, **84**, 442; *A.*, 451.

Useful structural work has been done on clays and clay minerals;[56] the different varieties are all based on the same $Al(OH)Si_2O_5$ sheets, arranged somewhat differently relatively to each other. The zeolites have been much studied, and the structure types proposed by Pauling (*Ann. Reports*, 1931, **28**, 302), based on various $(SiAl)O_2$ frameworks, have been confirmed and extended. The natrolite group has received the most attention. W. H. Taylor and W. Jackson [57] have determined the structure of natrolite, $Na_2Al_2Si_3O_{10},2H_2O$, and edingtonite, $BaAl_2Si_3O_{10},4H_2O$, the related meta-natrolite.[58] Ashcroftite,[59] mesolite,[60] and thomsonite [61] have been studied by other workers. E. Schiebold [62] has determined the structure of scapolite, E. Kozu [63] that of cancrenite, both zeolites containing CO_3. T. F. W. Barth [64] has studied the cuboctahedral structure of the sodalite group, and in conjunction with E. Posnjak, an interesting set of structures derived from cristobalite (see p. 400) by replacing half the Si^{4+} ions successively by Al^{3+} and Ca^{2+} without essential change of structure, the Na^+ ions needed for neutrality falling into the interstices of the structure, thus :

$(SiSiO_4)^0$ Cristobalite
$Na^+(AlSiO_4)^{1-}$ α-Carnegeite
$Na_2{}^+(CaSiO_4)^{2-}$

From a physical standpoint, the last structure is an orthosilicate with separate SiO_4 groups; crystallographically it has a $SiCaO_4$

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[56] J. W. Gruner, *Z. Krist.*, 1932, **83**, 75, 394; *A.*, 1932, 987; 1933, 45; 1933, **85**, 345; *A.*, 892; W. W. Jackson and J. West, *ibid.*, p. 160; *A.*, 451; U. Hofmann, K. Endell, and D. Wilm, *ibid.*, **86**, 340; see also (6), p. 380.

[57] *Ibid.*, 1933, **86**, 53; *A.*, 1004; W. H. Taylor, C. A. Meek, and W. W. Jackson, *ibid.*, **84**, 373; *A.*, 451; F. Halla and E. Mehl, *ibid.*, 1932, **83**, 140; *A.*, 1932, 987.

[58] M. H. Hey (with F. A. Bannister), *Min. Mag.*, 1932, **23**, 243; *A.*, 141.

[59] *Idem*, *ibid.*, 1933, **23**, 305; *A.*, 588.

[60] M. H. Hey, *ibid.*, p. 421.

[61] J. Wyart, *Compt. rend.*, 1931, **193**, 666; *A.*, 1932, 12.

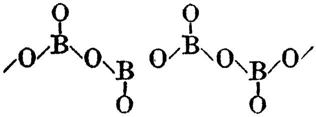
[62] E. Schiebold and G. Seumel, *Z. Krist.*, 1932, **81**, 110; *A.*, 1932, 218.

[63] S. Kôzu and K. Takané, *Proc. Imp. Acad. Tokyo*, 1933, **9**, 56, 105; *A.*, 558.

[64] *Z. Krist.*, 1932, **83**, 405; *A.*, 13; *Amer. Min.*, 1932, **17**, 466; *A.*, 482.

framework. The same transition of physical properties without change of crystal type is shown in the classical felspar series :

$$\text{Albite } Na(AlSi_3O_8)^{-} \longrightarrow \text{Anorthite } Ca(Al_2Si_2O_8)^{2-}$$

Complex Ions.—The work of the last two years, represented by over 100 papers, now makes it possible to review the types of complex ion in a wider and more rational scheme. In the first place, it is necessary to have a physical definition of a complex ion. The most general is : a charged group of atoms (closed or open) for each atom of which the forces attaching it to the group are greater than the forces attaching it to other atoms. Applying Pauling's rules to the simplest case of an ion of the type $B^{b+}X_n^{x-}$, we can see that this will always be a definite complex ion if $b/n > x/2$, for here the partial valency joining B to X, being greater than half the charge of X, no other valency can equal it. For oxy-ions the rule is simplest : an atom will always give a stable oxy-ion when its maximum valency is greater than its co-ordination number; *e.g.*, $C^{4+}O_3$, $P^{5+}O_4$, $I^{7+}O_6$. For fluoride ions, twice the valency must be greater than the co-ordination number; *e.g.*, $B^{3+}F_4$, $Si^{4+}F_6$. This rule gives a lower limit to the stability. Ions with weaker internal forces can, however, exist in favourable circumstances, *i.e.*, in the presence of large ions such as K˙ or Cl′. This is the case with co-ordinated ions of the type $Ni(NO_2)_6^{4-}$. Oxy-ions of this type, however, inevitably hydrolyse in water, *e.g.*, $SnO_6^{8-} \longrightarrow Sn(OH)_6^{2-}$. The ions for which $b/n = x/2$ tend to polymerise by sharing X atoms. Thus $(B^{3+}O_3)^{3-}$ gives  $/O/\overset{O}{\overset{|}{B}}\backslash O\backslash\underset{O}{\underset{|}{B}}\;O/\overset{O}{\overset{|}{B}}\backslash O\backslash\underset{O}{\underset{|}{B}}/O/$ = $(BO_2)'$ ions,[75] $(Si^{4+}O_4)^{4-}$ gives $(SiO_3)^{2-}$ chains, etc.; AlF_6^{3-} and WO_6^{6-} give framework structures. Where there are homopolar forces inside the ion, as in organic and quasi-organic ions, *e.g.*, the dithionate ion, the question of ionic stability merges into that of molecular stability.

Ions can be divided into mononuclear and polynuclear types. The former are of the general form $BX_n[n = (0),1,2,3,4,6]$; the latter consist of mononuclear ions bound together either (*a*) through X atoms (generally O), or (*b*) by covalent bonds between B atoms. The (*a*) type are represented by pyro- and per-ions and by the silicates; (*b*) by most organic ions. We limit by convention inorganic polynuclear ions to those which are fairly compact and symmetrical in structure. The simple mononuclear ions are symmetrical and linear, triangular, tetrahedral, or octahedral in shape. From them we can derive asymmetrical ions, either by removing X atoms, leaving a reduced ion with electron pairs (Zachariasen's principle, see *Ann. Reports*, 1931, **28**, 297), or by choosing different kinds of X atoms, by substituting, *e.g.*, F, S, or N for O in an oxy-ion.[65] The substitution of hydrogen to form a hypo-ion is an extreme case of this. The substitution of hydroxyl for oxygen or simple addition of hydrogen ion, leading to an acid ion or acid, does not change the form, or, in general, the symmetry of the ion, owing to the partial ionisation of the hydrogen in a hydrogen bond.

Two types of anomaly are apparent: those such as $SeBr_6^{2-}$ [66] and VF_6^{3-}, where the co-ordination is normal but the valency too low, and those such as WO_4^{2-} and OsO_4^0, where the valency is normal but the co-ordination too low.

Crystal-structural investigations have been able to throw considerable light on the nature of co-ordinated ions. A. Ferrari and C. Colla [67] have measured a series of salts containing the ions $[Co(NO_2)_6]^{3-}$ and $[Ni(NO_2)_6]^{4-}$. All form cubic face-centred cells, $a \approx 10$ Å., determined by the complex ions, various numbers of K, NH_4, Ba, Pb, etc., filling the interstices of the structure. Complete analysis was not attempted, but the published dimensions of the cell exclude, in the Reporters' opinion, the possibility of an electrostatic co-ordination $\mathrm{Co^+}\ {}^{{}^-\mathrm{O}}_{{}_-\mathrm{O}}\mathrm{N^+}$ and are only compatible with a covalent $\mathrm{Co—N}^{\mathrm{O}}_{\mathrm{O}}$ co-ordination.

The square planar configuration of the PtX_4 and PdX_4 ions, which can be considered as derived by removing two X atoms from the octahedral PtX_6 ion, has been fully confirmed by structure analyses on single crystals. R. M. Bozorth and L. Pauling [68] find planar configuration in $Mg_2PtCl_4,7H_2O$, while E. G. Cox in a series of papers [69] demonstrates it in $[Pd(NH_3)_4]Cl_2,H_2O$, $[Pt(NH_3)_4]Cl_2,H_2O$, $Pt(NH_3)_2Cl_2$,[70] and most clearly of all in the " green salt of Magnus " $[Pt(NH_3)_4][PtCl_4]$,[71] where the + and − planar ions are piled alternately along the tetrad axis of the crystal.

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[65] H. Seifert, *Z. Krist.*, 1932, **81**, 396; *A.*, 1932, 449.

[66] L. Sieg, *Z. anorg. Chem.*, 1932, **207**, 93; *A.*, 1932, 903; J. L. Hoard and B. N. Dickinson, *Z. Krist.*, 1933, **84**, 436; *A.*, 451.

[67] A. Ferrari and C. Colla, *Atti R. Accad. Lincei*, 1931, [vi], **14**, 435; *A.*, 1932, 483; *ibid.*, 1933, [vi], **17**, 390; *A.*, 666; cf. L. W. Strock, *Z. Krist.*, 1933, **86**, 42, 186, 270; *A.*, 1004, 1106, 1107.

[68] *Physical Rev.*, 1932, [ii], **39**, 537; *A.*, 1107.

[69] H. D. K. Drew, F. W. Pinkard, W. Wardlaw, and (in part) E. G. Cox, *J.*, 1932, 988, 1004; *A.*, 1932, 562 ; E. G. Cox, *ibid.*, p. 1912; *A.*, 1932, 797; E. G. Cox and G. H. Preston, *ibid.*, 1933, 1089; *A.*, 1040.

[70] F. Rosenblatt and A. Schleede, *Naturwiss.*, 1933, **21**, 178; *A.*, 342.

[71] E. Hertel and K. Schneider, *Z. anorg. Chem.*, 1931, **202**, 77; *A.*, 1932, 215; E. G. Cox, F. W. Pinkard, W. Wardlaw, and G. H. Preston, *J.*, 1932, 2527.

The structure of $K[Ag(CN)_2]$ has been studied by J. L. Hoard[72] and the $Ag(CN)_2$ groups found to be linear: this may be regarded as the last stage in removing substituents from a BX_6 complex. A similar linear arrangement has been found by H. M. Powell[73] in the dialkylthallium ions.

We are not yet in a position to classify the polynuclear ions. Those of the pyro-type sharing oxygen (or fluorine) are fairly familiar through the silicates. The most valuable addition is the three co-ordinated chain ion studied by W. H. Zachariasen[74] in calcium metaborate (see p. 407). The homopolar type is represented by the dithionate ion. G. V. Helvig,[75] G. Hägg,[76] and M. L. Huggins[77] are now all agreed that the ion consists of two pyramidal SO_3 groups joined point to point through the sulphur atoms in octahedral configuration. The hypophosphate ion, $O_3P{-}PO_3^{--}$, is probably isomorphous.[78] In connection with the heteropoly phosphotungstate ion $P(W_3O_{10})_4^{3-}$ mentioned in the Report (p. 105), it should be noted that, if the structure proposed is correct, it would require us to modify our conceptions of the laws of ionic structure, for one O^{2-} ion has as neighbours three W^{6+} ions and one P^{5+} ion, giving it an equivalent charge of 4¼ electrons instead of its usual two, while other oxygen ions receive a charge of only one electron.

The Salts.—Apart from information on the nature of ions, much work of crystal structural interest has been done on the salts. In ABX_3 compounds with flat ions, optical anisotropy is an important property, and has been much studied.[79] S. B. Hendricks[80] has published a full account of the changes of structure in ammonium nitrate due to ion rotation (see *Ann. Reports*, 1931, **28**, 291). V. M. Goldschmidt[81] has shown a long series of isomorphisms between

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[72] *Z. Krist.*, 1933, **84**, 231; *A.*, 215.

[73] H. M. Powell and (Miss) D. M. Crowfoot, *Nature*, 1932, **130**, 131; *A.*, 1932, 904.

[74] *Proc. Nat. Acad. Sci.*, 1931, **17**, 617; *A.*, 1932, 114; W. H. Zachariasen and G. E. Ziegler, *Z. Krist.*, 1932, **83**, 354; *A.*, 13.

[75] *Z. Krist.*, 1932, **83**, 485; *A.*, 13.

[76] *Z. physikal. Chem.*, 1932, [*B*], **18**, 327; *A.*, 1932, 986; *Z. Krist.*, 1932, **83**, 265; *A.*, 1932, 1079.

[77] *Ibid.*, 1933, **86**, 384.

[78] P. Nylen and O. Stelling, *Z. anorg. Chem.*, 1933, **212**, 169; *A.*, 664.

[79] W. H. Zachariasen, *Physical Rev.*, 1931, [ii], **37**, 1693; *A.*, 211; H. Brasseur, *Z. Krist.*, 1932, **83**, 493; *A.*, 10; K. S. Krishnan and A. C. Dasgupta, *Indian J. Physics*, 1933, **17**, 49; *A.*, 1109; P. Le Roux, *Compt. rend.*, 1933, **196**, 394; *A.*, 336; S. B. Hendricks, W. E. Deming, and M. E. Jefferson, *Z. Krist.*, 1933, **85**, 143; *A.*, 448.

[80] S. B. Hendricks, E. Posnjak, and F. C. Kracek, *J. Amer. Chem. Soc.*, 1932, **54**, 2766; *A.*, 1932, 986; J. M. Bijvoet and J. A. A. Ketelaar, *ibid.*, p. 625; *A.*, 1932, 445.

[81] V. M. Goldschmidt and H. Hauptmann, *Nach. Ges. Wiss. Göttingen*, 1932, 53; *A.*, 1932, 1079.

BO_3^{3-} and CO_3^{2-} ions. Thus $ScBO_3$, $InBO_3$, and $YtBO_3$ have the structure of $MgCO_3$, $CaCO_3$ (calcite) and $NaNO_3$, while $LaBO_3$ has the structure of $CaCO_3$ (aragonite), $BaCO_3$, and KNO_3.

New important type structures recently established are: ABX_3, NH_4NO_3[82] and $RbNO_3$;[83] A_2BX_4, Li_2SO_4,[84] $Na_2SO_4(Ag_2SO_4)$;[85] A_3BX_4, Li_3PO_4,[86] which shows great resemblance to Mg_2SiO_4 (olivine). Much work has been done on the apatite series[87] (see *Ann. Reports*, 1931, **28**, 297); the mineral constituent of bone and teeth is shown to be hydroxy-apatite, $Ca_3(OH)Ca_2(PO_4)_3$. The hydroxy-ion is very tightly held, and cannot be removed below 1400°. The structures of the beautiful copper carbonate minerals azurite, $Cu_3(OH)_2(CO_3)_2$, and malachite, $Cu_2(OH)_2CO_3$, have been studied by H. Brasseur.[88] The structures are complicated, and are true hydroxy-carbonates, not sandwich structures, $CuCO_3Cu(OH)_2$, as usually written. Other polyionic salts, such as northupite,[89] $Na_3MgCl(CO_3)_2$, and its related salts, have been studied with some success.

Our knowledge of water of crystallisation has been much increased by the determination of the structures of $Be(H_2O)_4SO_4$ and $Ni(H_2O)_6SO_4$ by C. A. Beevers and H. Lipson.[90] In each case the water molecules are co-ordinated to the cation, the co-ordination number being determined by the ionic size. The water molecules act as distributors of the ionic charge, each touching two oxygens of different SO_4 groups carrying an electrostatic valency of $\frac{1}{4}$ and $\frac{1}{6}$ in the beryllium and nickel sulphates respectively, each sulphate oxygen being accordingly touched by two water molecules belonging to different beryllium ions or three belonging to different nickel ions, so that in each case Pauling's rules are exactly obeyed. Other hydrates studied are $NaBr,2H_2O$, $NaI,2H_2O$,[91] $3CdSO_4,8H_2O$,[92] $Zn_{14}(OH)(AsO_4)_9,12H_2O$,[93] and finally $Na_7F(PO_4)_2,19H_2O$,[94] which crystal has a cubic cell, $a = 27{\cdot}86$ Å., containing 40 molecules of the above composition.

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[82] C. D. West, *J. Amer. Chem. Soc.*, 1932, **54**, 2256; *A.*, 1932, 903.

[83] L. Pauling and J. Sherman, *Z. Krist.*, 1933, **84**, 213; *A.*, 215.

[84] J. G. Albright, *ibid.*, 1932, **84**, 150; *A.*, 215.

[85] W. H. Zachariasen and G. E. Ziegler, *ibid.*, 1932, **81**, 92; *A.*, 1932, 218; W. H. Zachariasen and K. Herrmann, *ibid.*, **82**, 161; *A.*, 1932, 681.

[86] F. Zambonini and F. Laves, *ibid.*, **83**, 26; *A.*, 1932, 986.

[87] S. B. Hendricks, W. L. Hill, K. D. Jacob, and M. E. Jefferson, *Ind. Eng. Chem.*, 1931, **23**, 1413; *A.*, 1932, 359; S. B. Hendricks, M. E. Jefferson, and V. M. Mosley, *Z. Krist.*, 1932, **81**, 352; *A.*, 1932, 494; M. A. Bredig, H. H. Franck, and H. Füldner, *Z. Elektrochem.*, 1932, **38**, 158; *A.*, 1932, 469; A. Schleede, W. Schmidt, and H. Kindt, *ibid.*, p. 633; *A.*, 1932, 1217; G. Trömel, *Z. physikal. Chem.*, 1932, **158**, 422; *A.*, 1932, 481; R. Klement and G. Trömel, *Z. physiol. Chem.*, 1932, **213**, 263; *A.*, 296; M. A. Bredig, *ibid.*, 1933, **216**, 239.

[88] *Z. Krist.*, 1932, **82**, 111, 195; *A.*, 1932, 682.

[89] H. Shida and T. Watanabe, *Compt. rend.*, 1931, **193**, 1421; *A.*, 1932, 218; B. Gossner and I. Koch, *Z. Krist.*, 1931, **80**, 455; *A.*, 1932, 11; T. Watanabe, *Sci. Papers Inst. Phys. Chem. Res. Tokyo*, 1933, **21**, 40; *A.*, 802.

[90] *Z. Krist.*, 1932, **82**, 297; *A.*, 1932, 681; *ibid.*, **83**, 123; *A.*, 1932, 986; R .B. Corey and R. W. G. Wyckoff, *ibid.*, 1933, **84**, 477; *A.*, 451.

Molecular Crystals.

Although *X*-ray methods were from the beginning used to study molecular and, in particular, organic crystals, it is only in the last few years that they have begun to yield information of positive value to chemists. This was because, owing to the intrinsic difficulties of organic crystal analysis, the results obtained were in the case of simpler compounds too rough to do more than confirm the chemical evidence, while compounds where information of any kind would be of use were generally too complicated in structure to yield to the *X*-ray methods of the time.

Now, however, improvements in crystal analysis technique and a more extensive knowledge of the nature of molecules and of intra- and inter-molecular forces have changed all this, and results already achieved justify the claim of crystal analysis as an important and ultimately essential adjunct to structural chemistry.[95] Every stage in the crystal analysis of a molecular compound may be of value from the chemical standpoint. These stages may be summarised as follows :

(1) X-*Ray photograph of the crystal,* either as powder or single crystal. This is a very powerful means of identification. The angular positions and the intensities of the reflexions are equivalent to so many characteristics, each of the value of a melting point or other single physical determination. It has been used, for instance, in showing the substantial identity of adenine hydrochloride with a preparation of vitamin-B_4 (p. 424).

(2) *Determination of cell size.* This, in conjunction with a knowledge of the density, furnishes the most accurate method of absolute molecular-weight determination. The limitations of this method depend only on that of the density, which is difficult with very small or cracked crystals. The weight obtained is in general some simple exact multiple, *e.g.*, 2, 4, 6, 8, of the true molecular weight, but this multiple can be found at the next stage.

(3) *Determination of space group and molecular symmetry.* This

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[91] W. A. Wooster, *Nature*, 1932, **130**, 698; *A.*, 12.

[92] L. Egartner, F. Halla, and E. Schwarz, *Z. Krist.*, 1932, **83**, 422; *A.*, 12.

[93] J. Drugman and M. H. Hey (with F. A. Bannister), *Min. Mag.*, 1932, **23**, 175; *A.*, 1932, 1015.

[94] E. W. Neuman, *Z. Krist.*, 1933, **86**, 298; *A.*, 1107.

[95] J. D. Bernal, " Crystal Structure of Complex Organic Compounds " (a lecture), Metropolitan Vickers, Manchester.

is effected from X-ray photographs combined with a determination of polarity by piezo-[96] or pyro-electric methods,[97] or by etch figures. The first use to which this information can be put is the determination of the maximum molecular size. The minimum size cannot be determined, as all the molecules in a cell may not occupy crystallographically equivalent positions, even when no polymerisation has taken place. Thus, it is possible to distinguish between pure substances and molecular compounds, as in the cases of calciferol and quinhydrone (see pp. 423, 420). The actual molecular symmetry is, of course, of stereochemical importance in many cases, but here again the crystal analysis only gives a minimum symmetry, as molecules in general will not be able to pack so as to exhibit their highest symmetry (cf. benzene, p. 419).

(4) *General arrangement of molecules in the cell.* For this the X-ray evidence may be supplemented by evidence from physical properties—habit, cleavage, etc.—but most importantly by a knowledge of the optical or magnetic anisotropy of the crystal. In a molecular crystal where the intramolecular forces are strong and the intermolecular forces weak—as in nearly all organic crystals—the molecule behaves in the crystal very much as in a gas, and consequently the anisotropy of the crystal is a mere product of that of the individual molecules and of their mutual orientations.

Now the optical (or magnetic) anisotropy of a molecule is closely related to its shape—long molecules are positive, flat molecules negative, and round or compact molecules quasi-isotropic. If molecules pack parallel in a crystal, the optical character of the crystal is that of the molecules. If, as is more rarely the case, their axes lie in a plane, the character is inverted, *i.e.*, long molecules arranged at right angles give negative birefringence. If there is no selected common direction, quasi-isotropy results for every type of molecule.

It is nearly always possible from such indications to find the disposition of the molecules in the crystals, and hence their size and shape, even when the molecular structure is quite unknown, as has been done, *e.g.*, for vitamins B_1 and C (ascorbic acid, see p. 424). Once the size and shape of the molecule are known, many questions with respect to its structure can be answered. The method is essentially a negative one. Of proposed structures, some can be excluded as having inadmissible shapes, though at this stage it is impossible to be sure that a given admissible structure is the correct one. It was in this way that the new sterol formula was first deduced (see p. 423). The greatest difficulties are encountered where (*a*) the molecules are geometrically and optically quasi-isotropic, (*b*) intermolecular forces are large, as in poly-alcohols and acids, (*c*) the molecule is not rigid but protean in shape, owing to the existence of internal rotations. Thus the sugars and simple vegetable acids, where all these disadvantages occur together in varying degree, have not yielded anything significant to *X*-ray analysis, compared to that yielded by aromatic or paraffinoid types.

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[96] A. Hettich and H. Steinmetz, *Z. Physik*, 1932, **76**, 688; *A.*, 1932, 904.

[97] A. J. P. Martin, *Min. Mag.*, 1931, **22**, 519.

(5) *Determination of atomic positions.* Once the rough positions of molecules in a crystal are known, the exact positions of the atoms can be found by a laborious process of trial and error, so as to give a good agreement between observed and calculated intensities of reflexion.

(6) *Determination of electronic densities* (Fourier analysis) (see *Ann. Reports*, 1929, **26**, 280). Starting from approximate atomic positions, the phases of the diffracted beams can be found. This gives their complex amplitude, and hence by Fourier analysis a complete picture (usually a two-dimensional projection) of the electronic distribution can be obtained (see Figs. 1 and 2). From this, interatomic distances and valency angles can be read off, and these final values are, owing to the method of successive approximation used, independent of any original assumptions about the structure of the molecule.

This chain of operations is divided clearly into two parts, *viz.*, (1)—(4) and (5) and (6). The first is straightforward measurement, involving little calculation, and for any crystal species may take between a day and a week. The second calls for much experience and intuition, refined measurements of intensity, and heavy computations, running into several thousands of operations for one crystal, and the time taken must be reckoned by months. It is plain, therefore, that far fewer crystals can be determined by this complete *intensive* method than by rapid preliminary methods more adapted to *extensive* surveys. The two sides of the work are interdependent. Extensive surveys suggest which crystals will yield the most useful results if intensively analysed, while the results of intensive analysis provide data on intra- and inter-molecular distances useful in building up rough models of crystal structures, particularly in stage (4).

The chemical implications of these two aspects are also different. Intensive analysis provides fundamental information on stereochemistry and the nature of the chemical bond. It is one of the chief means of transformation from the classical qualitative, topological, chemistry of the nineteenth century to the quantum-mechanical, metrical chemistry of the present day. The extensive method is more closely connected with the practical development of chemistry in analysis and synthesis, particularly in dealing with complex biochemical problems. Here the chemist and the crystallographer must work in intimate collaboration. A large number of related substances and derivatives are prepared and examined, and from their crystallographic relations more can be discovered than from an elaborate analysis of any one of them. There is no doubt that, if chemists were more aware of the possibilities of these methods, there would result an enormous saving of time and effort.

Complete analyses of organic crystals are still rare. The work is a continuation of that of (Sir) W. H. Bragg at the Royal Institution, chiefly by J. M. Robertson and (Mrs.) K. Lonsdale. Including some earlier work, particularly that of R. W. G. Wyckoff, the only crystals for which complete analyses are available are shown in Table I.

TABLE I.

	Distances, Å.			
Crystal.	Intramolecular.		Intermolecular.	
Urea [16]	C—N	1·33	NH_2 . . . O=	3·20
	C=O	1·18		
Thiourea [17]	C—N	1·35	NH_2 . . . H_2N	3·85
	C=S	1·64	NH_2 . . . S=	3·45
Hexamethylbenzene [99]	C—C arom.	1·42		
	C—C aliph.–arom.	1·48		
Durene [35]	C—C arom.	1·41	CH_3 . . . H_3C	3·87
	C—C aliph.–arom.	1·47		
Naphthalene [47]	C—C arom.	$1·41_2$	CH . . . HC	3·60
Anthracene [48]	C—C arom.	1·41	CH . . . HC	3·77
p-Diphenylbenzene [44]	C—C between rings	1·48	CH . . . HC	3·92

With each crystal type are given the intramolecular distances which can be derived from it. These, together with the 1·54 Å. distance derived for the aliphatic bond from diamond, and the value 1·42 Å. for graphite, represent all the determinations of interatomic distances justifiable by *X*-ray measurement. Values are quoted by N. V. Sidgwick [98] for many other bonds, but, except where they depend on spectral data for symmetrical diatomic molecules, they are of the nature of predictions only. This is particularly the case for distances derived from electron diffraction, except for the simplest molecules of the BX_n type, where they are least liable to interpretative error. A summary of this work is given by L. Bru.[7]

The table also contains values of intermolecular distances, but these have not the same precise significance. For most organic molecular compounds covered by neon-like electronic orbitals (other forms occur only in compounds containing sulphur, chlorine, etc.) the distance between atoms in neighbouring molecules is determined primarily by residual (van der Waals) forces leading to a common

[98] "The Covalent Link in Chemistry," p. 81 *et seq.*

[99] (Mrs.) K. Lonsdale, *Proc. Roy. Soc.*, 1929, **123**, [*A*], 494; *A.*, 1929, 750.

value of about 3·6—4·0 Å. This is only slightly greater than the distance 3·41 Å. between the hydrogen-less molecular sheets of graphite. The presence of hydrogen atoms does not affect the distance much, as they are embedded in the electronic cloud of the atoms to which they are bound. If, however, they are part of a local dipole, as in hydroxy- or amino-groups, the interatomic distance may be reduced to 3—3·2 Å., or in the extreme case of acids, a hydrogen bond may reduce it to 2·55 Å.

All other work on molecular compounds is either of crystal physical interest, as showing how known molecules pack in a crystal, or of direct analytic interest, as leading to a structural formula which still remains to be proved by chemical methods. The results may be classified under : (1) Simple molecular compounds, including not only inorganic molecules, but organic compounds with compact molecules (pentaerythritol derivatives, etc.). (2) Long-chain molecules. (3) Ring molecules, simple, multiple, and condensed.

Simple Molecular Crystals.—Much work has been done on hydride structures.[1] Although the essential picture is that of close packing (*Ann. Reports*, 1931, **28**, 303), yet in almost very case there exist low-temperature forms with lower symmetry, usually tetragonal. The transitions in the solid are clearly due to dipole rotation, as has been shown by C. S. Hitchcock,[2] by the appearance of high dielectric constants at the transition temperatures, the only temperature at which the molecules are neither freely rotating nor fixed, and can thus respond to the electric field. Similar effects have long been known for ice and the alcohols, but curiously enough are not found for solid ammonia. M. Ruhemann[3] has shown that β-nitrogen (above 35° K.) is hexagonal close packed, as against the cubic close packing of α-nitrogen. The molecular polyhalides of the types BX_2, BX_4, BX_6, BX_8 have been studied in the solid by *X*-rays,[4] and in the liquid and vapour both by *X*-ray[5] and electron[6] methods. Electron methods have also been used by R. Wierl and L. Bru[7] for a whole set of simple molecules, hydrocarbons, halides, ethers, etc. In all these cases the structure determination depends on the interpretation of a small number of diffuse diffraction rings; it can only be of value in the simplest cases, and then only for the measurement of rough interatomic distances and valency angles. A very interesting application of electron diffraction is, however, shown by A. Stock and R. Wierl's[8] work on the compound $B_3N_3H_6$, which shows the same pattern as benzene, and should therefore be formulated as in (I). Other such cyclic inorganic compounds have been investigated.

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[1] G. Natta, *Mem. R. Accad. d'Italia*, 1931, **2**, [Chim., 3], 31; *A.*, 1932, 326; *Gazzetta*, 1933, **63**, 425; *A.*, 1003; B. Ruhemann and F. Simon, *Z. physikal. Chem.*, 1932, [*B*], **15**, 389; *A.*, 1932, 325.

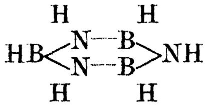
[2] C. S. Hitchcock and C. P. Smyth, *J. Amer. Chem. Soc.*, 1933, **55**, 1296, 1830; *A.*, 448, 663; K. Clusius, *Z. Elektrochem.*, 1933, **39**, 598; *A.*, 1000.

[3] *Z. Physik.*, 1932, **76**, 368; *A.*, 1932, 796.

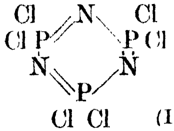
[4] O. Hassel and H. Kringstad, *Teknisk Ukeblad*, 1931, **78**, 230; *A.*, 1932, 326; *Z. physikal. Chem.*, 1932, [*B*], **15**, 274; *A.*, 1932, 325.

[5] R. W. James, *Physikal. Z.*, 1932, **33**, 737; *A.*, 12; L. Bewilogua, *ibid.*, p. 688; *A.*, 1932, 1078; W. van der Grinten, *ibid.*, p. 769; *A.*, 12; *ibid.*, **34**, 609; *A.*, 1003.

[6] L. O. Brockway and L. Pauling, *Proc. Nat. Acad. Sci.*, 1933, **19**, 68; *A.*, 341; H. Braune and S. Knoke, *Z. physikal. Chem.*, 1933, [*B*], **21**, 297; *A.*, 658; *Naturwiss.*, 1933, **21**, 349; *A.*, 658.



(I.)



(II.)

$(PNCl_2)_3$ and $(PNCl_2)_4$ have been shown by F. M. Jaeger[9] to have the structures like (II); S_4N_4 and $H_4S_4N_4$[10] are apparently more compact. Most interesting, however, is further light on the structure of sulphur.[11] E. Hertel[12] has shown, by examination of the trigonal molecular compounds $CHI_3,3S_8$, $AsI_3,3S_8$, that the S_8 molecules not only have a plane of symmetry but must be piled above each other in the direction of the *c*-axis at a mutual distance of 4·44 Å. This is only compatible with a disc-shaped molecule of external diameter ≈ 6·6 and thickness ≈ 4·4 Å. The most probable configuration is therefore a cyclic molecule derived from a cube flattened into a puckered octagon. A more careful analysis of this compound would give more information on the nature of the sulphur molecule than a study of the element itself.

G. Wagner and G. Dengel[13] have investigated the tetrahalides of pentaerythritol, finding simple cells with halogen atoms lying in planes, but the Reporters have reason to believe that the real structures are more complicated. The only other apparent exception found by *X*-ray analysis to the tetrahedral carbon atom is that of dibenzylidenepentaerythritol (see *Ann. Reports*, 1929, **26**, 304), the molecule of which was found by F. M. Jaeger to have three diad axes of symmetry.[14] One of the Reporters[15] has recently found that this is incorrect, as the crystal is really trigonal, not hexagonal, and in the molecule consequently only one diad was of symmetry, which is fully compatible with the tetrahedral carbon atom.

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[7] R. Wierl, *Ann. Physik*, 1932, [v], **13**, 453; *A.*, 1932, 670; J. Hengstenberg and L. Bru, *Anal. Fis. Quim.*, 1932, **30**, 341; *A.*, 1932, 798; L. Bru, *ibid.*, p. 483; *A.*, 1932, 1078; *ibid.*, 1933, **31**, 115; *A.*, 890.

[8] A. Stock and R. Wierl, *Z. anorg. Chem.*, 1931, **203**, 228; *A.*, 1932, 215.

[9] F. M. Jaeger and J. Beintema, *Proc. K. Akad. Wetensch. Amsterdam*, 1932, **35**, 756; *A.*, 116.

[10] F. M. Jaeger and J. E. Zanstra, *ibid.*, 1931, **34**, 782; *A.*, 1932, 797.

[11] J. J. Trillat and H. Forestier, *Bull. Soc. chim.*, 1932, [iv], **51**, 248 *A.*, 1932, 452.

[12] *Z. physikal. Chem.*, 1931, [*B*], **15**, 51; *A.*, 1932, 114.

[13] *Ibid.*, 1932, [*B*], **16**, 382; *A.*, 1932, 564.

R. W. G. Wyckoff and R. B. Corey have continued their work on urea[16] and its derivatives thiourea[17] and methylurea,[18] and have furnished valuable precise interatomic measurements (see Table I) and also F curves for carbon, nitrogen, and oxygen. F. V. Lenel[19] has continued his work on the polypeptides. Glutathione, the basic respiratory peptide, has been examined by J. D. Bernal,[20] who has shown that its three amino-acid units are arranged in a straight chain.

E. G. Cox[21] is making progress in the field of the sugars, but so far the difficulties have been too great to put forward any complete structure.

Long-chain Compounds.—A. Müller[22] has shown that the *cyclo*-paraffins C_nH_{2n} ($n = 12—30$) are essentially similar to the normal paraffins in structure, the flexible ring being drawn out under the influence of residual forces into a double chain with a small ring involving 1—3 carbon atoms at each end. The cross-section of the straight part of the ring is 37·5 Å.^{2}, almost exactly double that of a free paraffin, *viz.*, 18·3 Å.^{2}. More remarkable are the apparently greater intermolecular forces, especially in the low-carbon members : *cyclo*dodecane has, for instance, a density of 0·945 compared to 0·77 for dodecane. The rotation of the carbon chains of the paraffins in the solid state has been well established by his further work,[23] showing that it is complicated by other forms of polymorphism for hydrocarbons higher than C_{24}. These rotational forms have been studied optically for hydrocarbons and alcohols by N. Yannaquis[24] and J. D. Bernal,[25] where they appear as uniaxial hexagonal crystals.

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[14] See also " Handbuch v. Stereochemie."

[15] *Z. Krist.*, (in preparation).

[16] *Ibid.*, 1931, **81**, 102; *A.*, 1932, 218.

[17] *Ibid.*, p. 386; *A.*, 1932, 451. [18] *Ibid.*, 1933, **85**, 132; *A.*, 451.

[19] *Ibid.*, 1932, **81**, 224; *A.*, 1932, 451.

[20] *Biochem. J.*, 1932, **26**, 75; *A.*, 1932, 636.

[21] *J.*, 1932, 138, 2535; *A.*, 1932, 326, 1192; *Z. Krist.*, 1932, **84**, 45; *A.*, 216; E. G. Cox and T. H. Goodwin, *J.*, 1932, 1844; *A.*, 1932, 798; *Z. Krist.*, 1933, **85**, 462; *A.*, 892; G. W. McCrea, *Proc. Roy. Soc. Edin.*, 1932, **51**, 190; *A.*, 1932, 327.

[22] *Helv. Chim. Acta*, 1933, **16**, 155; *A.*, 267.

[23] *Proc. Roy. Soc.*, 1933, [*A*], **138**, 514; *Nature*, 1932, **129**, 436; *A.*, 451.

[24] *Compt. rend.*, 1933, **196**, 784; *A.*, 451.

[25] *Nature*, 1932, **129**, 870; *A.*, 1932, 798; *Z. Krist.*, 1932, **83**, 153; *A.*, 1932, 987.

E. Ott [26] has shown that, in general, mixtures of hydrocarbons and of alcohols show mixed crystals in the solid with occasional 1 : 1 molecular compounds. Separation can, however, be effected by distillation in high vacuum, as shown by (Miss) H. S. Gilchrist and (Miss) B. Karlik.[27] Other hydrocarbons, together with ketones and secondary alcohols, have been studied by S. H. Piper.[28] Polymorphism seems a general phenomenon both in these, and in the acids, esters, and salts studied by F. D. la Tour [29] and others.[30]

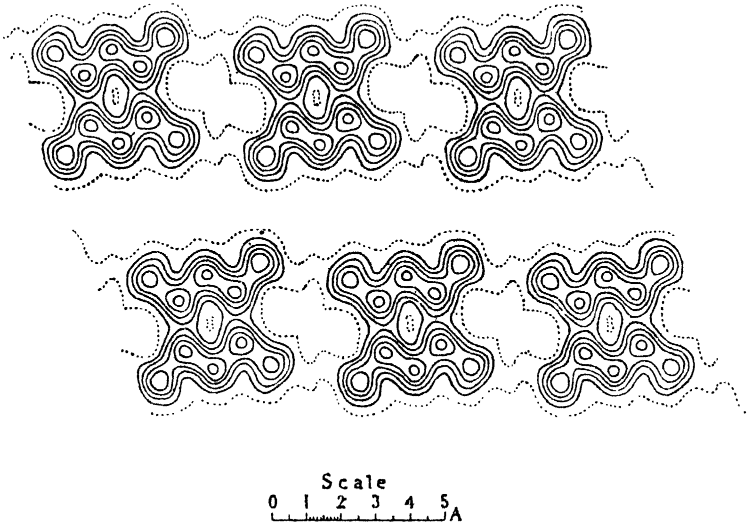

FIG. 1.—Projection along *b* axis showing mutual relation of molecules.

Most of this work has been done by measurement of long spacings only. We badly need a complete Fourier analysis of typical hydrocarbons, acids, etc.

Ring Compounds.—Ring compounds, particularly polyphenyl and condensed systems, have been found extremely amenable to crystal analysis, owing to the rigidity and large anisotropy of their molecules. The optical and magnetic anisotropy has been specially studied by S. B. Hendricks,[31] I. Obreimov,[32] and K. S. Krishnan.[33] Benzene itself has a structure, determined by E. G. Cox,[34] which is somewhat anomalous, being intermediate between that of a simple molecular crystal—the molecule centres are on a pseudo-cubic close-packed lattice—and that of a typical aromatic structure, as the molecules are not piled like plates but inclined almost at right angles to each other, giving a strongly positively birefringent crystal. The ring is

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[26] E. Ott and D. A. Wilson, *Science*, 1933, **78,** 16; *A.*, 896; E. Ott and F. B. Slagle, *J. Physical Chem.*, 1933, **37,** 257; *A.*, 342.

[27] *J.*, 1932, 1992; *A.*, 1932, 927.

[28] S. H. Piper, A. C. Chibnall, S. J. Hopkins, A. Pollard, J. A. B. Smith, and E. F. Williams, *Biochem. J.*, 1931, **25,**, 2072; *A.*, 1932, 250.

[29] *Compt. rend.*, 1932, **194,** 622; *A.*, 1932, 327; *Ann. Physique*, 1932, [x] **18,** 199; *A.*, 1932, 1192; J. Thibaud and F. D. la Tour, *J. Chim. physique*, 1932, **29,** 153; *A.*, 1932, 904.

[30] P. E. Verkade and J. Coops, *Proc. K. Akad. Wetensch. Amsterdam*, 1933, **36,** 76; *A.*, 559; D. Coster and A. v. d. Ziel, *ibid.*, 1932, **35,** 91; *A.*, 1932, 682; P. A. Thiessen and E. Ehrlich, *Z. physikal. Chem.*, 1932, [*B*], **19,** 299; *A.*, 116; *ibid.*, 1933, **165,** 453; *A.*, 1004; J. W. C. Phillips and S. A. Mumford, *J.*, 1932, 898; *A.*, 1932, 451; T. Malkin, *J.*, 1931, 2796; *A.*, 1932, 326; *Trans. Faraday Soc.*, 1933, **29,** 977; *A.*, 1107.

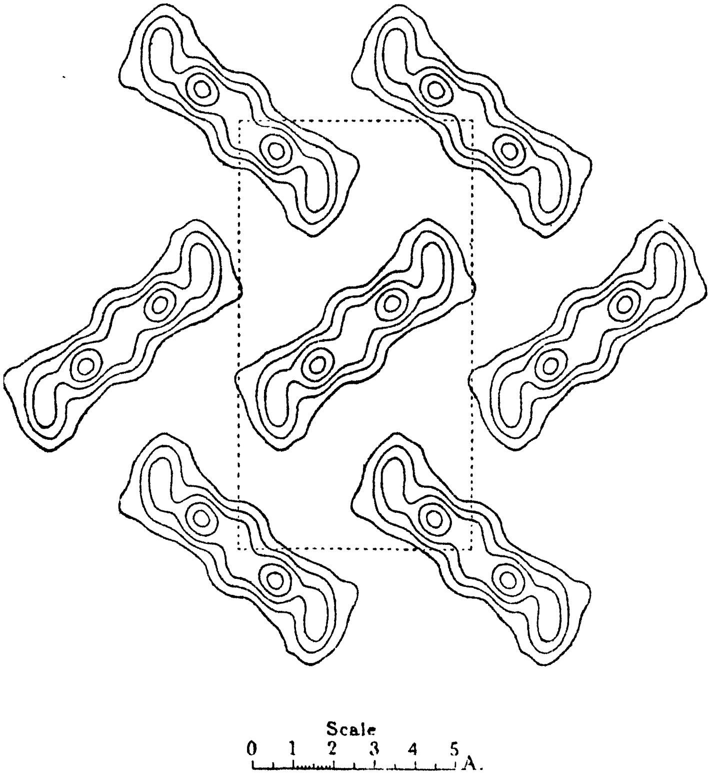

FIG. 2.—Projection along *c* axis showing mutual relation of molecules. Each contour line represents two electrons per Å.^{2}.

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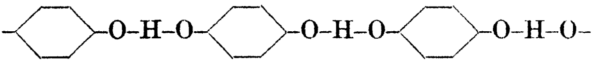
[31] S. B. Hendricks and M. E. Jefferson, *J. Opt. Soc. Amer.*, 1933, **23,** 299; *A.*, 1104.

[32] I. Obreimov and A. Prichotjko, *Physikal. Z. Soviet Union*, 1932, **1,** 203; *A.*, 1932, 674.

[33] *Nature*, 1932, **130,** 698; *A.*, 10.

[34] *Proc. Roy. Soc.*, 1932, [*A*], **135,** 491; *A.*, 1932, 451.

almost certainly planar, but the best evidence for this comes from the study of more complex aromatic structures, in particular durene, 1 : 2 : 4 : 5-tetramethylbenzene, for which a complete Fourier analysis was carried out by J. M. Robertson [35] (see p. 413 and Figs. 1 and 2). It is interesting to note that the mutual repulsion of methyl groups in the *o*-positions made them deviate from the radial orientation. Other benzene derivatives have been less thoroughly studied. *p*-Dichlorobenzene has been already mentioned (p. 382). The plane of symmetry reported for *m*-dinitrobenzene [36] (see *Ann. Reports*, 1931, **28**, 306) has now been shown by piezoelectric measurement [96] not to exist. Of particular interest are the structures of quinone, corrected from optical and magnetic measurements by K. S. Krishnan and S. Banerjee,[37] and that of quinhydrone determined by O. R. Foz and J. Palacios.[38] The cell is monoclinic, space group $C_{2h}^5 - P2_1/n$, but in it there is only one molecule of quinone, and one of quinol, and these must be derivable from each other by a symmetry axis. The only conclusion is that here we have to do with no molecular compound, but with a new type of chain polymeride held together by hydrogen bonds :



This would explain both the peculiar oxidation–reduction properties of the substance, and its extreme optical pleochroism. The crystals are practically black for vibration directions along the macromolecule, even when transparent and showing Newton's colours for the other vibration. In vapour and solution, ring polymerisation may take the place of chain polymerisation.

The most complex benzene derivative studied is the mineral mellite, $Al_2C_{12}O_{12},18H_2O$, which has a large tetragonal cell with 16 molecules.[39] E. Halmöy and O. Hassel's work in *cyclo*hexane derivatives [40] shows fairly conclusively that here the atoms do not lie in a flat ring.

The essential nature of polyphenyl structures has now been established. Diphenyl itself has been measured by J. Dhar [41] and by L. W. Pickett [42] by the *X*-ray method, and the molecular orientation determined optically by K. S. Krishnan.[43] L. W. Pickett[44] has also published a Fourier analysis of *p*-diphenylbenzene (cf. Hertel),[45] and preliminary results for *p*-diphenyldiphenyl[40] (bis-diphenylyl). In these compounds the structure found shows that the benzene rings are flat hexagons which in any one molecule lie in the same plane. The value for the distance C–C between the rings was 1·48 Å., *i.e.*, intermediate between those observed in aromatic and in aliphatic carbon atoms. The implication is that the Ph–Ph bond does not easily admit of rotation. This is further confirmed by the analysis of *s*-triphenylbenzene by (Mrs.) K. Lonsdale,[46] where all rings lie in a plane.

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[35] *Proc. Roy. Soc.*, 1933, [*A*], **141**, 594; *A.*, 1108.

[36] S. B. Hendricks and G. E. Hilbert, *J. Amer. Chem. Soc.*, 1931, **53**, 4280; *A.*, 1932, 327.

[37] *Nature*, 1933, **131**, 653; *A.*, 557; W. A. Caspari, *Proc. Roy. Soc.*, 1932, *A*, **136**, 82; *A.*, 1932, 682.

[38] *Anal. Fís. Quím.*, 1932, **30**, 421; *A.*, 1932, 904.

[39] T. F. W. Barth and C. J. Ksanda, *Amer. Min.*, 1933, **18**, 8; *A.*, 928.

[40] *Z. physikal. Chem.*, 1932, [*B*], **16**, 234; **17**, 258; *A.*, 1932, 451, 798.

[41] *Indian J. Physics*, 1932, **7**, 43; *A.*, 1932, 798.

[42] *Nature*, 1933, **131**, 513; *A.*, 451.

In a similar way J. M. Robertson[47] has established the structure of the basic condensed ring systems naphthalene[47] and anthracene,[48] and with J. Iball[49] extended this study to chrysene and 1 : 2 : 5 : 6-dibenzanthracene. Condensed ring systems form flat rigid molecules, which with increasing number of rings tend to pack more and more in parallel sheets approximating to the structure of graphite.

Stilbene, tolane, and *o*-azotoluene have been described by M. Prasad.[50] The crystals all show similarities with those of azobenzene. The —N=N— and —C≡C— are equivalent in length within the errors of experimental measurement, —C=C— is somewhat longer. To this group also belong the aromatic disulphides and diselenides measured by L. Egartner, F. Halla, and R. Schacherl.[51] The series included diphenyl and dibenzyl disulphides and diselenides, and dibenzoyl disulphide. The parameters of the sulphur and the selenium atoms were determined, and their radii from the distance between the two centres found to be in both cases 1·19 Å., rather larger than the values S = 1·04, Se = 1·13 Å. found in the elements. This is probably the half length of the S–S (Se–Se) single bond. The straight character of dibenzyl derivatives is maintained for similar multiple-linked phenyl groups such as dibenzylidenebenzidine or diethyl *pp'*-xylylidenebisaminocinnamate, as shown by the work of J. D. Bernal [52] and K. Herrmann [53] on the crystal structures of substances giving rise to liquid crystals.

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[43] *Nature*, 1932, **130**, 313; K. S. Krishnan, B. C. Guha, and S. Banerjee, *Phil. Trans.*, 1933, [*A*], **231**, 2315; *A.*, 340.

[44] *Proc. Roy. Soc.*, 1933, [*A*], **142**, 333; *A.*, 1235.

[45] E. Hertel and G. H. Römer, *Z. physikal. Chem.*, 1933, [*B*], **21**, 292; *A.*, 666.

[46] *Nature*, **1934**, **133**, 67.

[47] *Proc. Roy. Soc.*, 1933, [*A*], **142**, 674.

[48] *Z. Krist.*, 1933, **84**, 321; *A.*, 216; *Proc. Roy. Soc.*, 1933, [*A*], **140**, 79; *A.*, 558.

[49] *Nature*, 1933, **132**, 750.

[50] *Phil. Mag.*, 1933, [vii], **16**, 639; *A.*, 1107; M. Prasad and K. V. Desai, *ibid.*, 1932, [vii], **13**, 600; *A.*, 327.

[51] *Z. physikal. Chem.*, 1932, [*B*], **18**, 189; *A.*, 1932, 987.

E. Hertel [54] and his co-workers have examined a number of the substitution products of trinitrobenzene, and also several molecular compounds.[55] It seems a pity that in this work the optical properties of the crystals generally are not measured, as these should assist in the structure determination far more than the theories of molecular packing put forward. This is particularly the case with the interesting observations on colour dimorphism in which one might correlate change of colour with the actual alteration in the mutual arrangements of chain and ring systems rather than with chemical interaction. Among condensed ring systems, J. Hengstenberg and J. Palacios [56] have shown that the two anthracene molecules in dianthracene are probably linked at the 9 : 9′-positions, the anthracene ring system being slightly bent at the centre to enable this linking to take place.

There has been a certain increase in *X*-ray measurements taken rather for purposes of identification of the compounds than for structure determinations. A very complete series is that of derivatives of ephedrine and ψ-ephedrine,[57] where the measurements should prove sufficiently complete to lead ultimately to the exact structures.

In the last two years a number of important groups of biochemical compounds, the sterols, the bile acids, the female and the male sexual hormones, as well as other substances, pregnandiol, digitoxin, bufotoxin, etc., have been shown to be based on a common condensed ring system. The establishment of this common skeleton was due initially to *X*-ray investigation of one of its more complex members, calciferol (vitamin D). The chemical proofs of the new sterol formula are dealt with in another part of these Reports (p. 198), but it is here of some importance to state precisely how the methods of crystal analysis were of use in settling difficult points or indicating possible lines of attack. The following summary is arranged in roughly chronological order.

[52] J. D. Bernal and (Miss) D. Crowfoot, *Trans. Faraday Soc.*, 1933, **29**, 1032; *A.*, 1107.

[53] K. Herrmann and A. H. Krummacher, *Z. Krist.*, 1932, **81**, 317; *A.*, 1932, 450.

[54] E. Hertel and G. H. Römer, *Z. physikal. Chem.*, 1933, [*B*], **22**, 267; *A.*, 1004.

[55] E. Hertel and K. Schneider, *ibid.*, 1932, [*B*], **18**, 436; *A.*, 1932, 1080; E. Hertel and G. H. Römer, *ibid.*, [*B*], **19**, 228; *A.*, 116; *ibid.*, 1933, [*B*], **22**, 280; *A.*, 1004.

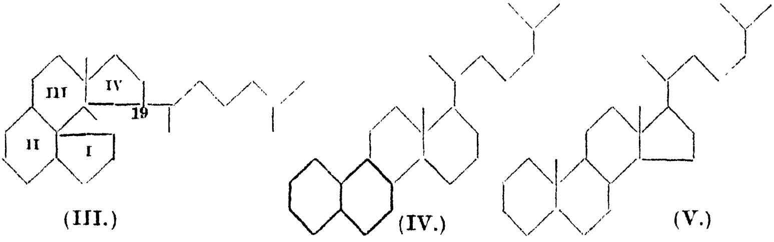
[56] *Anal. Fis. Quim.*, 1932, **30**, 5; *A.*, 1932, 327.

[57] K. Brückl, *Z. Krist.*, 1932, **81**, 219; *A.*, 1932, 451; B. Gossner and H. Neff, *Z. Krist.*, 1933, **85**, 370; *A.*, 892; *ibid.*, **86**, 32; *A.*, 1004.

(1) The first crystal structural investigation of calciferol and its related compounds [58] and of cholesterol and ergosterol showed (*a*) on the evidence of the space group and number of molecules in the cell, that calciferol was a simple substance (see p. 412); (*b*) on evidence of cell size and optically determined molecular orientation, that the sterol molecule must occupy a space 5 × 7·2 × 17—20 Å. and must form in the crystal a double layer similar to that of long-chain alcohols. This showed that the accepted skeleton (III) must be wrong in at least two essential points: (i) the sharing of one carbon atom by rings I, II, and III, for this would lead to a much thicker molecule, and (ii) the attachment of the long chain at C_{19}, which would lead to a much shorter molecule than that observed. Further, (iii) the double layer pointed to a hydroxyl group placed terminally in the molecule. (This was confirmed later by an examination of ψ-cholesterol, which with a hydroxyl in ring II shows no double layer.)

(2) Meanwhile, a concurrent but fortuitously undertaken investigation of œstrin [59] pointed strongly to a structure with a phenanthrene nucleus of approximately the same molecular width and thickness. A little later it was apparent that pregnandiol,[60] which was already known to be related through the bile acids to the sterols, had also very similar molecular dimensions.

(3) These were the considerations from crystallography that, added to the serious chemical defects of the old sterol formula, led Rosenheim and King [61] to propound the new formula (IV) subsequently amended to (V), which accounted for all the features occurring in the crystal analysis.



(III.) (IV.) (V.)

Subsequent work has consisted, for the most part, in attempting to fill in details of the structure.

(4) The general *trans*-nature of the skeleton probable from the

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[58] J. D. Bernal, *Nature*, 1932, **129**, 277; *A.*, 1932, 327.

[59] J. D. Bernal, *Chem. and Ind.*, 1932, **51**, 259; cf. C. Gaudefroy, *Compt. rend.*, 1932, **195**, 523; *A.*, 1932, 1079.

[60] J. D. Bernal, *Chem. and Ind.*, 1932, **51**, 466; *A.*, 1932, 736; *Nature*, 1932, **129**, 721; *A.*, 1932, 658.

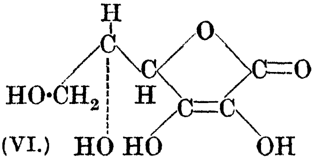
[61] *Chem. and Ind.*, 1932, **51**, 464; *A.*, 1932, 736.

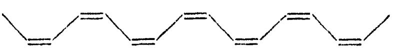
thinness of the molecule was made more certain by an examination of *cis*- and *trans*-hexahydrochrysenes [62] synthesised by G. R. Ramage and R. Robinson, of which only the former showed no resemblance to a sterol derivative.

(5) The attempt to settle the nature, 5- or 6-membered, of ring IV has led to much work on the hydrocarbons derived from the sterols, in particular Diels's hydrocarbon $C_{18}H_{16}$. While it has been impossible to determine its structure, *X*-ray and optical methods have shown that it is not *cyclo*pentenophenanthrene,[63] and its resemblance to retene suggested the structure γ-methyl*cyclo*pentenophenanthrene. This was subsequently synthesised by E. Bergmann [64] and by G. A. R. Kon [65] and appears to be indistinguishable from the natural product.

(6) Much further work is in progress, in particular on the position of the double bonds. Here, both *X*-ray and optical theory [66] suggest but cannot prove that in ergosterol these lie in rings I and/or II. This is still in opposition to current chemical opinion.

Similar but less extensive work has been done on vitamins B_1, B_4,[67] and C. The structural formula of the last, now known as *l*-ascorbic acid (VI), was established, as in the case of the sterols, by a close collaboration of E. G. Cox's [68] crystal analysis with orthodox chemical methods.


(VI.)


(VII.)

In another important group, the polyenes, which includes carotene and vitamin A, a very complete study of methyl bixin has been carried out by H. Waldmann and E. Brandenberger.[69] These crystals have remarkable optical properties; the refractive indices of 1·630, 1·649, and >2·63—for which last vibration direction the crystal is almost black—fix the orientation of the molecule absolutely in the cell, and determine the nature of the molecule as a *cis*-polyene chain. This is presumably the chain of the completely polymerised rubber which has recently been obtained in single crystals by E. W. Washburn.[70]

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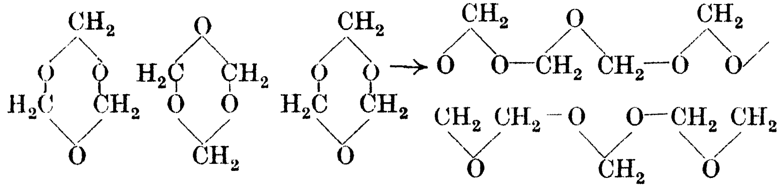
[62] J. D. Bernal, *Chem. and Ind.*, 1933, **52**, 288.
[63] *Ibid.*, p. 729.
[64] E. Bergmann and H. Hillemann, *Ber.*, 1933, **66**, 1302; *A.*, 1154.
[65] *Chem. and Ind.*, 1933, **52**, 951.
[66] J. D. Bernal and T. M. Lowry, *Chem. and Ind.*, 1933, **52**, 10.
[67] J. D. Bernal and (Miss) D. Crowfoot, *Nature*, 1933, **131**, 911; *A.*, 768.
[68] *Nature*, 1932, **130**, 205; *A.*, 1932, 987.
[69] *Z. Krist.*, 1932, **82**, 77; *A.*, 1932, 682.

Fibre Structures.

A discussion of *X*-ray work on fibres requires a separate report: here we can only mention the most salient advances of the last two years. The whole subject has been admirably summed up by W. T. Astbury in "Fundamentals of Fibre Structure" (Oxford, 1933), and in shorter articles.[71]

The simplest fibre substances studied are the polyoxymethylenes. Crystallographic research on these, chiefly carried out by H. W. Kohlschütter and L. Sprenger[72] and E. Sauter,[73] has been able to show precisely how the polymerisation takes place, and has probably given the clue to the mechanics of polymerisation in all chain polymeride systems. Trioxymethylene crystallises in the hexagonal system with six-ring molecules arranged in order along the hexad axis :



On exposure to light in the presence of free formaldehyde, nuclei appear in the crystals, and starting from them fibrous polyoxymethylene appears, the fibre axis lying along the hexagonal axis, and with a 9-fold repeat pattern corresponding to the 6-fold repeat of the trioxymethylene. All that has happened, quite clearly, is an interchange of homopolar bonds proceeding in a "zip" fashion, made possible by the previous apposition of the appropriate molecules of the ring polymeride by crystal forces. In this way the crystals of ring polymerides autocatalyse their transformation to chain polymerides. This mechanism may prove of very general application. The apposition of chain polymeride molecules necessary to form fibres may be produced by flow and shear, as has been very beautifully shown by W. H. Carothers and J. W. Hill[74] for poly-esters. A thread of glassy poly-ester is instantaneously converted by strain into an oriented fibre.

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[70] *Physical Rev.*, 1931, [ii], **38**, 1790; *A.*, 1933, 371.

[71] *Science Progress*, Oct. 1933, 210; W. T. Astbury and H. J. Woods, *Phil. Trans.*, 1933, [*A*], **232**, 333; *J. Text. Inst.*, 1932, **23**, 17; *A.*, 1932, 451.

[72] *Z. physikal. Chem.*, 1932, [*B*], **16**, 284; *A.*, 1932, 721; cf. W. Kern, *Kolloid-Z.*, 1932, **61**, 308; *A.*, 14.

[73] *Z. physikal. Chem.*, 1932, [*B*], **18**, 417; *A.*, 1932, 1080; *ibid.*, 1933, [*B*], **21**, 161, 186; *A.*, 666; cf. *Z. Krist.*, 1932, **83**, 340; *A.*, 13.

[74] *J. Amer. Chem. Soc.*, 1932, **54**, 1579; *A.*, 1932, 601.

Of carbohydrate polymerides, the literature on cellulose is too voluminous even to be referred to, but some understanding of the mechanism of cellulose formation in Nature has been derived by the study of the cell walls of single cells of the alga *Valonia ventricosa*,[75] which have been shown to consist of a double spiral network of cellulose chains intersecting nearly at right angles to give a " multiply " structure of maximum strength. This is probably the case in all vegetable cell walls, save that in elongated fibre cells the angle is reduced to a few degrees. In wood, K. Freudenberg [76] has shown that the cellulose network is reinforced by interstitial lignin.

The starches have been much studied, particularly by J. R. Katz [77] and his co-workers. The difference between starch and cellulose is due to the steric inability of the former, derived from α-glucose, to build straight chains leading to a nearly amorphous structure.

The most generally significant advance, however, is in our understanding of the essential nature and classification of proteins. W. T. Astbury has now shown that the protein, besides its characteristic peptide chain which can exist in the α-(contracted) or β-(expanded) form, has also a characteristic thickness and width. The thickness 4·65 Å. between NH and CO in neighbouring chains is roughly the same for all proteins, but the width corresponds to bonding between the side chains, and consequently varies with their length, being only 4·5—6·1 Å. in silk fibrin,[78] and up to 9·8 Å. in keratin. Further, the side chains can remain unattached, as in the soluble proteins like ovalbumen,[79] can be attached by ionic linkages in the gelatins,[80] myosin, and muscle,[81] or by permanent peptide or $^{-}S^{-}S^{-}$ linkages in the sclero-proteins such as keratin,[82] giving rise to a semi-rigid ladder-like structure. The extremely complex physical properties of the proteins, particularly their behaviour on swelling [83] with water [84] or adsorption on surfaces,[85] have already been qualitatively analysed by this model. Here we have undoubtedly the key to the mechanism of movement, if not to the very existence, of living matter.

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[75] W. T. Astbury, T. C. Marwick, and J. D. Bernal, *Proc. Roy. Soc.*, 1932, [*B*], **109**, 443; *A.*, 1932, 438.

[76] *Papier-Fabr.*, 1932, **30**, 189; *A.*, 1932, 605; R. Thiessen, *Ind. Eng. Chem.*, 1932, **24**, 1032; *A.*, 216.

[77] J. R. Katz and A. Weidinger, *Rec. trav. chim.*, 1931, **50**, 1133; *A.*, 1932, 149; J. R. Katz and J. C. Derksen, *Naturwiss.*, 1932, **20**, 851; *A.*, 14; M. Samec and J. R. Katz (with R. Klemen), *Z. physikal. Chem.*, 1933, **163**, 291; *A.*, 464.

[78] O. Kratky and S. Kuriyama, *Z. physikal. Chem.*, 1931, [*B*], **11**, 363; *A.*, 1931, 415; I. Sakurada and K. Hutino, *Sci. Papers Inst. Phys. Chem. Res. Tokyo*, 1933, **21**, 266; *A.*, 1108; J. R. Katz and A. de Rooy, *Naturwiss.*, 1933, **21**, 559; *A.*, 1004; *Rec. trav. chim.*, 1933, **52**, 742; *A.*, 893.

[79] W. S. Miller, K. G. Chesley, H. V. Anderson, and E. R. Theis, *J. Amer. Leather Chem. Assoc.*, 1932, **27**, 174; *A.*, 807.

[80] J. R. Katz, J. C. Derksen, and W. F. Bon, *Rec. trav. chim.*, 1931, **50**, 1138; *A.*, 1932, 123; J. J. Trillat, *Ann. Inst. Pasteur*, 1932, **48**, 400; *J. Chim. physique*, 1932, **29**, 1; *A.*, 1932, 466; O. Gerngross, K. Herrmann, and R. Lindemann, *Kolloid-Z.*, 1932, **60**, 276; *A.*, 1932, 1088; K. Hess and C. Trogus, *Biochem. Z.*, 1933, **262**, 131; *A.*, 893; W. T. Astbury and W. R. Atkin, *Nature*, 1933, **132**, 348; *A.*, 1108.

[81] G. Boehm and H. H. Weber, *Kolloid-Z.*, 1932, **61**, 269; *A.*, 14.

After the proteins, the lipoids are of the greatest biological interest. Here we find liquid-crystal structures playing an important rôle, as emphasised by F. Rinne.[86] This is particularly the case in nerve,[87] which has been studied by *X*-rays in active, narcotised, and degenerate states. Thus the applications of *X*-ray technique are already passing the boundary of biochemistry into physiology and pathology.

Liquids and Glasses.

The methods of *X*-ray analysis of liquids and amorphous solids developed by Debye and Prins (see *Ann. Reports*, 1929, **26**, 306) have been the basis for an extensive study of types of liquid structure. The two characteristics of a liquid are (*a*) the close contact between the molecules, leading to a relatively dense approximately close-packed structure; (*b*) the irregular nature of the packing over distances more than a few molecular diameters. Both these characters are modified by the temperature and the nature of the molecules. Higher temperatures produce rotary and translatory molecular movements, but molecular clustering still occurs up to and even slightly above the critical point, as shown by the work of F. H. W. Noll [88] on ether. The effect of the nature of the molecules is more varied. *X*-Ray analysis distinguishes between small-angle diffraction due to intermolecular, and large-angle diffraction due to intramolecular, interference. Further, the small-angle diffraction is either normal, indicating close packing, or abnormal, indicating a looser arrangement of molecules, generally brought about by dipole attractions. The analysis of these offers greater difficulty as it can only be done indirectly by assuming a mean molecular distribution, and calculating the diffraction to compare with that observed. It has, however, been attempted in one case, that of water,[89] where the basic arrangement is tetrahedral (quartz-like) rather than close-packed.

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[82] W. T. Astbury, *Trans. Faraday Soc.*, 1933, **29**, 193; *A.*, 216.

[83] J. B. Speakman and M. C. Hirst, *ibid.*, p. 148; *A.*, 227; W. T. Astbury and T. C. Marwick, *Nature*, 1932, **130**, 309; *A.*, 1932, 1080.

[84] (Miss) D. J. Lloyd and H. Phillips, *Trans. Faraday Soc.*, 1933, **29**, 132; *A.*, 226.

[85] A. H. Hughes and E. K. Rideal, *Proc. Roy. Soc.*, 1932, [*A*], **137**, 62; *A.*, 909.

[86] *Trans. Faraday Soc.*, 1933, **29**, 1016; *A.*, 1108; *Z. Krist.*, 1932, **82**, 379; *A.*, 1932, 798.

[87] H. Handovsky, *Kolloid-Z.*, 1933, **62**, 21; *A.*, 313; G. Boehm, *ibid.*, p. 22; *A.*, 313.

[88] *Physical Rev.*, 1932, [ii], **42**, 336; *A.*, 14.

Greater anisotropy of molecules leads to clumping in parallel aggregates, as occurs in nematic liquid crystals which show when oriented a fibre diagram. Finally they may arrange themselves in layers, generally curved, as in smectic liquid crystals which show one set of crystal plane reflexions. (Between these and true crystals are still other intermediate stages; see below.) The general scheme is shown below:

1. Atomic liquids: Hg, Na, K, Rb, Cs.[90]
2. Close-packed molecular liquids: Ga_2,[91] CCl_4,[91] $C_2H_4Cl_2$,[92] $(C_2H_5)_2O$,[88] S_8.
3. Associated molecular liquids: H_2O,[93] $C_6H_{13}\cdot OH$.[94]
4. Nematic liquids.[95]
5. Smectic liquids: thallium stearate.[96]

The precise intimate structure of liquids is still in dispute. According to G. W. Stewart,[97] a liquid consists of a mass of small quasi-crystallites, the so-called cybotactic groups, containing 10—100 molecules, not necessarily permanent, and separated by a number of unattached molecules. Another view [98] contends that these aggregates have only a statistical and not a physical existence, and that every molecule in the liquid is immediately surrounded by the same quasi-regular arrangement of molecules.

We have no space to discuss the great developments of the past two years in the study of liquid crystals (see *Ann. Reports*, 1931, **28**, 280). Luckily the whole subject is amply covered by the Faraday Society's volume "Liquid Crystals and Anisotropic Melts." [99] The most important facts that have emerged are the clear distinction between nematic liquids where neighbouring molecules are merely oriented in parallel, and smectic liquids where they are also arranged in regular planes, inside of which they either form a two-dimensional liquid (true smectic) or are arranged in lattices (crystalline smectic), which are still free to move over each other. The urious focal conic structures exhibited by smectic crystals have been shown by (Sir) W. H. Bragg[1] to be an equilibrium structure for molecular layers lacking rigidity.

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[89] J. D. Bernal and R. H. Fowler, *J. Chem. Physics*, 1933, **1**, 515.

[90] J. T. Randall and H. P. Rooksby, *Nature*, 1932, **130**, 473; *A.*, 1932, 1192.

[91] H. Menke, *Physikal. Z.*, 1932, **33**, 593; *A.*, 1932, 986.

[92] F. Ehrhardt, *ibid.*, p. 605; *A.*, 1932, 987.

[93] E. Amaldi, *Physikal. Z.*, 1931, **32**, 914; *A.*, 1932, 11.

[94] W. C. Pierce, *Physical Rev.*, 1931, [ii], **38**, 1409; *A.*, 1932, 12.

[95] K. Herrmann, A. H. Krummacher, and K. May, *Z. Physik*, 1931, **73**, 419; *A.*, 1932, 214.

[96] K. Herrmann, *Trans. Faraday Soc.*, 1933, **29**, 972; *A.*, 1107.

[97] *Indian J. Physics*, 1933, **7**, 603; *A.*, 891.

[98] Cf. *Trans. Faraday Soc.*, 1933, **29**, 1070 *et seq.*

[99] *Ibid.*, p. 883; J. D. Bernal, *Nature*, 1933, **132**, 86.

Glasses have plainly the same internal molecular structure as liquids : they differ by their relative immobility, with the consequent appearance of rigidity, or more correctly, of a long characteristic time for plastic flow. (Liquids also have an internal rigidity, as shown by B. V. Deriagin,[2] but the characteristic time is short.) Thermodynamically, glasses differ from undercooled liquids by the absence of internal equilibrium, as discussed by F. Simon,[3] E. Berger,[4] and G. Tammann.[5] The liquid–glass transformation is not sharp, but inside a small temperature range the slope of various property–temperature curves changes markedly. Gels are diphasic systems, one of which is generally a glass, though sometimes crystalline.[6]

W. H. Zachariasen[7] has discussed the conditions under which glasses are formed, equating them with the possibility of forming three-dimensional frameworks. This, in the case of ionic glasses, occurs when, in the notation of p. 407, $b/n \approx x/2$, *e.g.*, for boric anhydride, silica, tungsten trioxide, beryllium fluoride. Glasses may also be expected where metallic and homopolar structures have approximately the same energy, *e.g.*, for selenium and arsenic.

The actual atomic arrangements in vitreous silica have been determined by B. Warren;[8] it is simply a completely irregular three-dimensional network of SiO_4 tetrahedra sharing oxygens. Other glasses have also been studied by *X*-rays.[9]

The utilisation of electronic and protonic waves for crystal, liquid, and molecular analysis has grown into too large a subject to be discussed in this report (see *Ann. Reports*, 1929, **26**, 284). The main methods and results, however, have been described in W. L. Bragg's "Crystalline State." Owing to the low penetrating power of electrons, the chief applications have been to thin films, metal surfaces, and free molecules, regions where X-rays, for the opposite reason, give little information. Thus, the two methods are very happily complementary.

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[1] *Trans. Faraday Soc.*, 1933, **29**, 1056; *A.*, 1105.

[2] *Physikal. Z. Soviet Union*, 1933, **4**, 431.

[3] *Z. anorg. Chem.*, 1931, **203**, 219; *A.*, 1932, 217.

[4] *J. Amer. Ceram. Soc.*, 1932, **15**, 647; *A.*, 115.

[5] G. Tammann and A. Elbrächter, *Z. anorg. Chem.*, 1932, **207**, 268; *A.*, 1932, 996.

[6] J. C. Derksen, *Collegium*, 1932, 838; *A.*, 125.

[7] *J. Amer. Chem. Soc.*, 1932, **54**, 3841; *A.*, 12; *Physical Rev.*, 1932, [ii], **39**, 185; *A.*, 1107.

[8] *Z. Krist.*, 1933, **86**, 349.

[9] M. Hirata, *Sci. Papers Inst. Phys. Chem. Res. Tokyo*, 1932, **18**, 237; *A.*, 1932, 1015.

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